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(54) 【発明の名称】 インクジェット用インクおよびこれを用いたインクセット、並びにインクジェット記録方法

## (57) 【要約】

【課題】 カラーブリード、およびコゲーションの発生を確実に抑制し、かつ保存性も向上させ、さらに、インクヘッドの構成の複雑化を回避して、サーマルジェット方式の画像形成装置に好適に用いることができるインクジェット用インクを提供する。

【解決手段】 水性溶媒中に、ベタイン構造を有する水溶性染料およびカチオン界面活性剤を含んでなるカラーインクと、水性溶媒中に、黒色顔料を含み、かつアルカリ性を示すブラックインクとを用いる。特に、カラーインクはベタイン構造を有しているので、酸性条件下でも非常に安定した状態となり、コゲーションを生じず、保存性も向上させることができる。また、カラーインクとブラックインクとの間で酸-アルカリ反応が生じるので、ブラックインクが迅速に定着するため、カラーブリードを抑制することができる。

**【特許請求の範囲】**

【請求項1】水性溶媒中に、ベタイン構造を有する水溶性染料と、カチオン界面活性剤とを含んでなることを特徴とするインクジェット用インク。

【請求項2】上記カチオン界面活性剤は、アミン類の酢酸塩であることを特徴とする請求項1記載のインクジェット用インク。

【請求項3】pHが4以上7未満の範囲内に調整されていることを特徴とする請求項1または2記載のインクジェット用インク。

【請求項4】水性溶媒中にベタイン構造を有する水溶性染料およびカチオン界面活性剤を含んでなるカラーインクと、水性溶媒中に黒色顔料を含み、かつアルカリ性を示すブラックインクとを含むことを特徴とするインクジェット用インクセット。

【請求項5】上記カラーインクのpHは4以上7未満の範囲内であるとともに、上記ブラックインクのpHは7を超えて10未満となる範囲内であることを特徴とする請求項4記載のインクジェット用インクセット。

【請求項6】上記ブラックインクに含まれる黒色顔料は、アニオン顔料であることを特徴とする請求項4または5記載のインクジェット用インクセット。

【請求項7】上記ブラックインクには、黒色顔料を分散させる分散剤、および画像形成時に被記録材上に黒色顔料を定着させる結着剤の少なくとも一方が含まれていることを特徴とする請求項4、5、または6記載のインクジェット用インクセット。

【請求項8】上記請求項4ないし7の何れか1項に記載のインクジェット用インクセットを用いて、被記録材上に画像を形成することを特徴とするインクジェット記録方法。

**【発明の詳細な説明】****【0001】**

【発明の属する技術分野】本発明は、インクジェット方式の画像形成装置に用いられるインクに関するものであり、特に、カラーブリードの発生だけでなく、いわゆるコゲーションの発生を抑制し、さらに保存性も向上させることによって、高品位な画像形成を可能にするインクジェット用インクに関するものである。

**【0002】**

【従来の技術】ハードコピー用の画像形成装置としては種々の方式のものが提案され、実用化されている。中でも、インクジェット方式（液滴噴射記録方式）の画像形成装置（インクジェットプリンタ）は、高品位の画像形成が可能である上に、装置全体のコストを低く抑えることができるため、特に、高品位のカラー画像を形成する用途で好ましく用いられている。

【0003】ここで、上記インクジェット方式においては、従来より、カラーブリードまたはブリーディングと呼ばれる問題点が発生することが知られている。

【0004】つまり、インクジェット方式では、カラー画像を得るためには、通常、水を主溶媒とする複数の色のインクを、紙などの被記録材上に重ねて記録している。このとき、先に被記録材上に吐出されたある色のインクが定着する前に、次々と他の色のインクが吐出されて重ねられることになる。そのため、異なる色の境界となる部分では、異なる色のインク同士が拡散したり移動したりして各色の境界線が不明確となる現象、すなわちカラーブリードまたはブリーディング（以下、カラーブリードで統一）が発生する。

【0005】上記カラーブリードが発生すると、異なる色の間にじみが生じたり各色が不均一に混じり合った状態となるため、画像品位を低下させる。特に、画像形成においては、ブラックが最も重要な色となるが、このブラックと他の色との間でカラーブリードが生ずると、ブラックの画像の境界がにじんだりぼやけたりして、非常に画像品位を低下させることになる。

【0006】そこで、このカラーブリードの発生を抑制する技術が、従来から種々提案されている。たとえば、特開平5-202328号公報および特開平6-106375号公報には、多価金属塩をインクの凝固に用いることによってカラーブリードを抑制する技術が開示されている。

【0007】具体的には、特開平5-202328号公報では、カルボキシル基を少なくとも1つ有する染料を含むインクと、多価金属塩とを用い、先に多価金属塩溶液を被記録材上に供給した後、インクを供給している。これによって、被記録材上でインクが急速に乾燥してカラーブリードの発生が抑制されるとともに、乾燥後のインクの耐水性も向上させることができる。

【0008】また、特開平6-106735号公報では、イエロー、マゼンタ、シアンの各インクが、浸透性を付与する界面活性剤または浸透性溶媒と塩とを含有しており、かつブラックのインクが上記塩の作用により増粘または凝集を起こす成分を含有している。これによって、カラーブリードの発生を抑制するとともに、画像濃度の均一性を向上させ、さらにブラックの品位を向上させることができる。

【0009】さらに、特開平8-209049号公報においては、ゲル形成種を含む第1組成物と、該第1組成物と反応してゲルを形成するゲル化開始種とを含む第2組成物を用いる技術が開示されている。この技術では、各組成物を隣接している領域に吐出し、各領域間においてゲルを形成させることによってカラーブリードの発生を抑制している。

【0010】また、特開平9-207424号公報においては、上記多価金属塩を用いることに加えて、インクに顔料および樹脂エマルジョンを含有させる技術が開示されている。上記樹脂エマルジョンは多価金属イオンとの相互作用により、着色成分の浸透を抑制し、被記録材

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への定着を促進する。また、樹脂エマルジョンは、被記録材上で被膜を形成して印刷物の耐擦性を向上させることもできる。さらに顔料を用いれば、インク中の着色成分の浸透をより抑制することが可能になる。このような作用によって、カラーブリードがさらに一層抑制される。

【0011】加えて、特開平11-349878号公報においては、ブラックインクとカラーインクとの間でイオンの相互作用を生じさせ、カラーブリードを抑制する技術が開示されている。この技術では、ブラックインクにアニオン顔料を含有させるとともに、カラーインクにカチオンを供給する成分（たとえばカチオン界面活性剤やカチオン塩）を含有させている。その結果、ブラックインク・カラーインク間でのイオンの相互作用が生じて、カラーブリードの発生が抑制される。

【0012】ところで、上記インクジェット方式の中でも、インクをノズル内のヒータで瞬時に加熱し、発生した気泡の圧力でノズルからインクを吐出させるサーマルジェット方式においては、上記カラーブリード以外に、コゲーションと呼ばれる問題点が発生することも知られている。

【0013】コゲーションとは、一般には、インク中の着色成分の熱分解により生じる物質や、インク中に含まれる微量の無機不純物、凝集物などが上記ヒータ上に付着・堆積し、その結果ヒータによるインク加熱が十分に実施できなくなり、安定したインクの吐出が持続しなくなる現象をいう。このコゲーションの発生には、特に、インク中の無機イオン（特に金属イオン）が大きな影響を及ぼすことが知られている。

【0014】たとえば、インクの組成にカチオン塩が含まれていると、該カチオン塩を形成する無機イオンなどが、ヒータ上で加熱されることによって、インクの他の組成と反応して不溶物が形成されることがある。このような不溶物がヒータ上に付着・堆積すると上記コゲーションが発生する。

【0015】

【発明が解決しようとする課題】ここで、上述した従来の技術では、カラーブリードをある程度抑制することはできるものの、上記コゲーションの発生を回避することが困難であるという問題点を招来している。

【0016】まず、多価金属塩をインクの凝固に用いる技術では、この多価金属塩のイオンがコゲーションを発生させてしまい、インクが正常にヘッドから吐出できなくなる。したがって、上記特開平5-202328号公報、特開平6-106375号公報、および特開平9-207424号公報の各技術では、多価金属塩を含有する反応液とインクとをそれぞれ別々に被記録材（紙）上に吐出して、該被記録材上で反応液とインクとを混合している。しかしながら、このように二種類の成分を別々に吐出する技術では、インクヘッドの構造が複雑になっ

てしまい、製造コストを上昇させる上に、画像形成の制御やメンテナンスも煩雑化させるという問題点を招来する。

【0017】一方、特開平8-209049号公報においては、第1・第2組成物に含まれるゲル形成種やゲル化開始種の組み合わせがコゲーションを発生させる原因となるため、やはりサーマルジェット方式に適用するには実用性に欠けるという問題点を招来する。

【0018】さらに、特開平11-349878号公報においては、上述した多価金属塩やゲル形成種・ゲル化開始種などといったコゲーションを発生させる要因となる物質をほとんど含んでいない。したがって、理論上は、コゲーションの発生もカラーブリードの発生も抑制することは可能である。ところが、この技術では、カチオン塩またはカチオン界面活性剤を用いることが必須である。これら物質は酸性条件下で安定であるが、アルカリなどを配合すると水に不要な物質を生成して効力を失うので、インクは酸性を示さなければならない。

【0019】インクが酸性を示すと、通常、色成分として含まれる染料や顔料は凝固したり沈殿したりし易くなり、その結果、インクの保存性や安定性に大きな問題を生ずることになる。このようにインクの保存性や安定性が低下すると、画像形成時にサーマルジェットのヘッド内で凝固や沈殿が生じる可能性も高くなり、結果として、コゲーションの発生を確実に抑制することはできない。

【0020】さらに、上記特開平11-349878号公報の技術では、インクの諸特性を最適化するためにpHを調整することについては触れているものの、具体的なpHの範囲などについては全く言及されていない。したがって、上記技術においては、染料や顔料の凝固や沈殿による保存性の低下に関しては何ら具体的な対策がとられていない。

【0021】一般に、たいいていの染料や顔料にはスルホ基やカルボキシル基が含まれている。そのため、これら染料や顔料を含むインクにカチオン界面活性剤やカチオン塩が加えられると、上記スルホ基やカルボキシル基とカチオン界面活性剤やカチオン塩とが容易に酸-アルカリ反応を起こし、インク中に凝集物が生じる。したがって、上記カチオン界面活性剤やカチオン塩などを含むインクは、酸-アルカリ反応によって凝集物が発生し易い組成となっている。

【0022】このようなインクでは、単にインク中で凝集物が発生し易いだけでなく、時間の経過とともに、凝集物の数が増加したりサイズが大きくなる。そのため、長期間放置するだけでも、凝集物が発生してインクカートリッジ内のインク流路に詰まり易くなってインクの吐出を妨げる上に、この凝集物が、上記ヒータ上に付着・堆積してコゲーションを引き起こすため、ヒータによるインクの安定した加熱が妨げられて、インクの吐出が不

安定になる。

【0023】つまり、カチオン界面活性剤やカチオン塩を含む組成のインクは、単にコグーションを起し易いだけではなく、経時的に凝集物が発生するために、インクの保存性も低下することになる。その結果、最終的には、インクの吐出能力が不可逆的に低下して、インカートリッジの寿命も短縮化されるという問題点を招来する。

【0024】本発明は上記問題点に鑑みてなされたものであって、その目的は、カラーブリードやコグーションの発生を確実に抑制し、かつ保存性も向上させ、さらに、インクヘッドの構成の複雑化を回避して、サーマルジェット方式の画像形成装置に好適に用いることができるインクジェット用インクを提供することにある。

【0025】

【課題を解決するための手段】本発明者らは、上記問題点を鑑みて鋭意検討した結果、カラーインクおよびブラックインク間でイオンの相互作用を生じさせるとともに、カラーインクとして用いられるインクに含まれる染料として、ベタイン構造を末端に有するものを用いることによって、カラーブリードだけでなく、コグーションの発生も抑制することができる上に、保存性も向上させることが可能であることを見出し、本発明を完成するに至った。

【0026】すなわち、本発明にかかるインクジェット用インクは、上記の課題を解決するために、水性溶媒中に、ベタイン構造を有する水溶性染料と、カチオン界面活性剤とを含んでなることを特徴としている。

【0027】通常、カチオン界面活性剤がある条件下では上記インクは酸性となり、水溶性染料が凝固する問題点が発生するが、上記構成によれば、上記水溶性染料がベタイン構造を有しているので、酸性条件下でも非常に安定した状態となり、インクの保存性が向上する。しかも、上記インクには、金属塩やゲル化に関わる成分などがほとんど含まれていない。そのため、ノズルで加熱されてもコグーションをほとんど生じない。さらに、上記構成では、アルカリ性のインクと組み合わせ使用すれば、カラーブリードを抑制することもできる。

【0028】上記インクジェット用インクにおいては、上記カチオン界面活性剤が、アミン類の酢酸塩であることが好ましい。

【0029】上記構成によれば、アミン類の酢酸塩を用いることによって、十分なインクの表面張力の調整効果が得られる上に、コグーションの発生をより一層確実に回避することができる。

【0030】上記インクジェット用インクにおいては、そのpHが4以上7未満の範囲内に調整されていることが好ましい。

【0031】上記構成によれば、インクのpHが上記範囲内に調整された状態、すなわち弱酸性の状態にあり

ば、特にアルカリ性のインクと組み合わせることによって、カラーブリードの抑制効果をより一層向上させることができる。

【0032】また、本発明にかかるインクジェット用インクセットは、上記の課題を解決するために、水性溶媒中に、ベタイン構造を有する水溶性染料およびカチオン界面活性剤を含んでなるカラーインクと、水性溶媒中に、黒色顔料を含み、かつアルカリ性を示すブラックインクとを含むことを特徴としている。

【0033】上記構成によれば、まず、ブラックインクは、アルカリ性条件下で安定して黒色顔料を分散（懸濁）した状態にある一方、カラーインクは、酸性条件下で、ベタイン構造を有する水溶性染料が安定した状態にある。しかも、これら各インクには、金属塩やゲル化に関わる成分などがほとんど含まれていない。そのため、これらインクがノズルで加熱されてもコグーションの発生が抑制される。

【0034】また、ブラックインクとその他のカラーインクとが被記録材上で会合すると、アルカリ性のブラックインクと酸性のカラーインクとが酸-アルカリ反応を起して、これをきっかけとして、黒色顔料は被記録材上で容易かつ迅速に沈殿する。その結果、黒色顔料がカラーブリードを起こさずに定着する。

【0035】さらに、上記ブラックインクおよびカラーインクは、非常に安定した状態にあるので、画像形成の頻度が小さく、画像形成動作の間の時間が長いような場合であっても、黒色顔料や水溶性染料が凝固したり沈殿することがない。そのため優れた保存性を発揮することができる。

【0036】上記カラーインクのpHは4以上7未満の範囲内であるとともに、上記ブラックインクのpHは7を超えて10未満となる範囲内であることが好ましい。

【0037】上記構成によれば、ブラックインクおよびカラーインクの双方のpHが好ましい範囲に調整されることになるので、上記酸-アルカリ反応をより一層効果的に発生させることができる。

【0038】上記インクジェット用インクセットにおいては、上記ブラックインクに含まれる黒色顔料が、アニオン顔料であることが好ましい。

【0039】上記構成によれば、黒色顔料がアニオン顔料であるため、ブラックインクにおける黒色顔料の分散性がより向上する。その結果、ブラックインクの保存性をより一層向上させることができる。また、アニオン顔料の分散状態は、ブラックインク中におけるイオン電荷のバランスに大きく依存することになるため、ブラックインク-カラーインクによる酸-アルカリ反応によってイオン電荷のバランスが崩れると、アニオン顔料は容易に凝集したり沈殿したりすることになる。したがって、カラー画像形成におけるブラックインクのカラーブリードを効果的に抑制することができる。

【0040】上記インクジェット用インクセットにおいては、上記ブラックインクには、黒色顔料を分散させる分散剤、および画像形成時に被記録材上に黒色顔料を定着させる結着剤の少なくとも一方が含まれていることが好ましい。

【0041】上記構成によれば、分散剤の存在によって、黒色顔料の分散性がさらに向上する。その結果、ブラックインクの保存性を向上させ得るとともに、コゲーションの発生をさらに一層抑制することができる。また、結着剤の存在によって、黒色顔料の定着がより迅速かつ確実となるので、カラーブリードの発生もさらに一層抑制することができる。特に、上記分散剤および結着剤の双方を含んでいれば、コゲーションおよびカラーブリードの抑制効果をより向上させることができるとともに、保存性もより向上させることができる。

【0042】本発明にかかるインクジェット記録方法は、上述したインクジェット用インクセットを用いて、被記録材上に画像を形成することを特徴としている。

【0043】上記方法によれば、アルカリ性条件下で安定なブラックインクと、酸性条件下で安定なカラーインクとが、被記録材上で会合すると、ブラックインクとカラーインクとが酸-アルカリ反応を起して、ブラックインクのイオン電荷のバランスが低下する。そのため、均一に分散している黒色顔料が、非常に容易に沈殿（または凝固）し、黒色顔料は被記録材上で容易かつ迅速に沈殿する。その結果、黒色顔料がカラーブリードを起こさずに定着することになって、カラーブリードを抑制することができる。

【0044】しかも、従来のように多価金属塩やゲル化のための成分などを含んでいないためコゲーションの発生も抑制できるとともに、ブラックインクおよびカラーインクが非常に安定した状態にあるので保存性も向上することになる。さらに、多価金属塩とインクとを別々に吐出するような構成を採用する必要がないため、インクヘッドの構成を複雑化を回避して低コスト化できるとともに、そのメンテナンスも簡素化することができる。

【0045】

【発明の実施の形態】本発明の実施の一形態について説明すれば、以下の通りである。なお、本発明はこれに限

【0046】本発明にかかるインクジェット用インクは、特に、カラー画像形成のためのカラーインクとして好適に用いられるものであり、水性溶媒中に、ベタイン構造を有する水溶性染料と、カチオン界面活性剤とを含んでなるものである。そのため、カラーブリードおよびコゲーションの発生を抑制し、高い保存性を発揮しつつ、高品位の画像を良好に形成することができる。

【0047】また、本発明にかかるインクセットは、少なくとも一種類のカラーインクと一種類のブラックイン

クとを含んでなるものであり、該ブラックインクは、水性溶媒中に黒色顔料を含む組成を必須とし、かつアルカリ性を示すインクである一方、上記カラーインクは、水性溶媒中にベタイン構造を有する水溶性染料と、カチオン界面活性剤とを含む組成を必須とし、かつ酸性を示すインクである。

【0048】すなわち、本発明にかかるインクジェット記録方法は、カラーインクとブラックインクとを使用してカラー画像を形成するものであり、カラーインクとブラックインクとはそれぞれ別の組成となっている。

【0049】本発明にかかるカラーインクには、必須成分として水溶性染料が含まれているが、該水溶性染料はベタイン構造を有している。

【0050】本発明におけるベタイン構造とは、広義のベタインが有する構造、すなわち、分子内塩で両性イオンを形成し、溶液中で両性イオンとして存在する化合物が有する構造を指す。換言すれば、本発明で言うベタインとは、一つの分子内に、たとえば第4級アンモニウム塩基などのカチオン（陽イオン）構造（分子内塩基性基とする）と、たとえばカルボキシル基やスルホ基などのアニオン（陰イオン）構造（分子内酸性基とする）とを有する分子内塩型化合物として定義される。

【0051】したがって、本発明における水溶性染料は、上記ベタイン構造を有しているために、分子内塩で両性イオンを形成しており、水性溶媒が酸性であってもアルカリ性であっても安定して該水性溶媒に溶解する。その結果、水溶性染料が凝固したり沈殿したりするといった問題点の発生を回避することができる。

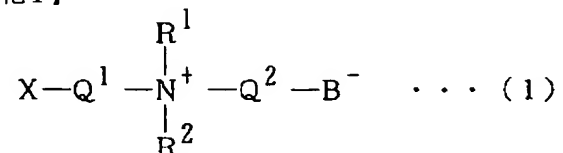
【0052】上記水溶性染料としては、上記ベタイン構造を有していれば特に限定されるものではないが、具体的には、たとえば、各種水溶性染料において、該水溶性染料の基本構造をXとした場合に、分子内塩基性基として第4級アンモニウム構造が含まれる次の2種類の構造を有するものを挙げることができる。

【0053】i) 鎖式化合物

次の構造式（1）で示すような、鎖式（側鎖があってもよい）の第4級アンモニウム構造において窒素原子に結合している4つの原子団のうち、基本構造Xの水溶性染料を含む原子団と、分子内酸性基B<sup>-</sup>を含む原子団とがそれぞれ1つずつ含まれている構造。

【0054】

【化1】

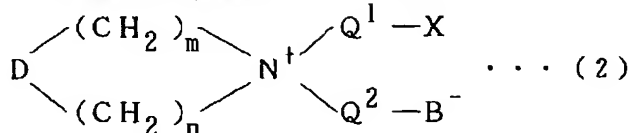


【0055】ただし、上記構造式（1）においては、R<sup>1</sup> および R<sup>2</sup> は、それぞれ独立して、炭素数1～4のアルキル基を示し、Q<sup>1</sup> は、無くてもよいが、あるいは、

酸素原子、炭素数 1・2 のアルキレン構造またはオキシアルキレン構造を示し、 $Q^2$  は、炭素数 1~4 のアルキレン構造またはオキシアルキレン構造を示す。

【0056】ii) 環式化合物

次の構造式(2)で示すような、含窒素単環式複素環化



【0058】ただし、上記構造式(2)においては、 $n$  および  $m$  は、それぞれ独立して1または2の整数であり、 $Q^1$  は、無くてもよいが、あるいは、酸素原子、炭素数1・2のアルキレン構造またはオキシアリキレン構造を示し、 $Q^2$  は、炭素数1~4のアルキレン構造またはオキシアリキレン構造を示し、 $D$  は、酸素原子、炭素数1・2のアルキレン構造を示す。

【 0 0 5 9 】 上記基本構造 X で表される水溶性染料の好適な例としては、たとえば、イエローの染料としては、アシッドイエロー 23、ダイレクトイエロー 86 などが、マゼンタの染料としては、リアクティブレッド 58、リアクティブレッド 120、リアクティブレッド 180、アシッドレッド 52、アシッドレッド 214 などが、シアン染料としては、アシッドブルー 7、アシッドブルー 9、ダイレクトブルー 86、ダイレクトブルー 199 などが挙げられるが、特に限定されるものではなく、カラーインクとして発色させたい色に応じて、従来公知の水溶性染料を適宜選択することができる。

【0060】上記分子内酸性基 $B^-$ は、酸性を示す原子団であれば特に限定されるものではないが、たとえばスルホ基( $-SO_3^-$ )やカルボキシ基( $-COO^-$ )を好ましく挙げることができる。

【0061】上記R<sup>1</sup> またはR<sup>2</sup> で示される炭素数1～4のアルキル基としては、たとえば、メチル基(CH<sub>3</sub>—)、エチル基(C<sub>2</sub>H<sub>5</sub>—)、プロピル基(C<sub>3</sub>H<sub>7</sub>—)、ブチル基(C<sub>4</sub>H<sub>9</sub>—)、イソプロピル基((CH<sub>3</sub>)<sub>2</sub>CH—)が挙げられる。

【0062】上記Q<sup>1</sup>で示される炭素数1・2のアルキレン構造としては、メチレン(—CH<sub>2</sub>—)、エチレン(—C<sub>2</sub>H<sub>4</sub>—)が挙げられ、オキシアルキレン構造としては、オキシメチレン(—OCH<sub>2</sub>—)、オキシエチレン(—OC<sub>2</sub>H<sub>4</sub>—)が挙げられる。また、上記Q<sup>2</sup>で示される炭素数1～4のアルキレン構造としては、メチレン(—CH<sub>2</sub>—)、エチレン(—C<sub>2</sub>H<sub>4</sub>—)、トリメチレン(—C<sub>3</sub>H<sub>6</sub>—)、テトラメチレン(—C<sub>4</sub>H<sub>8</sub>—)が挙げられ、オキシアルキレン構造としては、オキシメチレン(—OCH<sub>2</sub>—)、オキシエチレン(—OC<sub>2</sub>H<sub>4</sub>—)、オキシトリメチレン(—OC<sub>3</sub>H<sub>6</sub>—)、オキシテトラメチレン(—OC<sub>4</sub>H<sub>8</sub>—)が挙げられる。

化合物の第4級アンモニウム構造における窒素原子に、基本構造Xの水溶性染料を含む原子団と分子内酸性基B<sup>-</sup>を含む原子団とがそれぞれ1つずつ結合している構造。

【 0 0 5 7 】

【化2】

【0063】上記Dで示される炭素数1・2のアルキレン構造としては、上記メチレン、エチレンの各構造が挙げられる。このDは酸素原子でもよいことから、上記構造式(2)における含酸素単環式複素環化合物としては、具体的には、ピロリジン、ピペリジン、ヘキサメチレンイミン、モルホリンなどが挙げられる。

【0064】なお、上記の例では、分子内塩基性基として最も一般的な第4級アンモニウム構造を例に挙げたが、本発明においては、上記ペタイン構造を形成できるものであれば、分子内塩基性基がその他の塩基構造であってもよいことはいうまでもない。

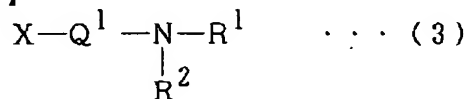
【0065】上記（１）または（２）の構造式を有するベタイン構造の水溶性染料の製造方法としては、上記基本構造Ⅹで表される水溶性染料に対して、従来公知の方法、具体的には、たとえば『全訂版 新・界面活性剤入門』（著：藤本武彦、三洋化成工業株式会社）の第８６頁～第８８頁に記載されている方法などによってベタイン構造を導入する方法が挙げられる。

【0066】具体的には、たとえば、分子内塩基性基として上記第4級アンモニウム構造を、分子内酸性基B<sup>-</sup>としてスルホ基(—SO<sub>3</sub><sup>-</sup>)を選択する場合は、次に説明する方法が好適に用いられる。

【0067】まず、上記基本構造Xの水溶性染料に対して、従来公知の方法によって第3級アミン（第三アミン）構造を導入し、次の構造式（3）に示すような鎖式水溶性染料アミンか、または構造式（4）に示すような複素環式水溶性染料アミンを得る。なお、水溶性染料が元からアミン構造を含んでいればそのまま使用することができる。

【 0 0 6 8 】

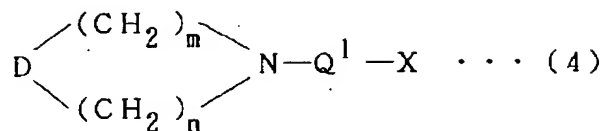
【化3】



【 0 0 6 9 】

【化4】

11



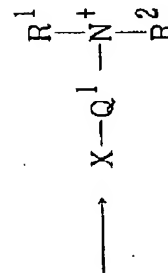
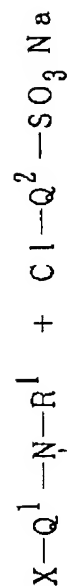
【0070】次に、上記何れかの水溶性染料アミンと、炭素数1～4のクロロアルキルスルホン酸ナトリウム、またはクロロアルキルオキシルスルホン酸ナトリウム（何れの化合物も  $\text{Cl}-\text{Q}^2-\text{SO}_3\text{Na}$  で表す）とを、必要なら適当な溶媒中に添加・混合して、60～80℃で数時間攪拌しながら次の反応式（5-1）または（5-2）の反応を進行させ、第3級アミン構造にスルホ基を導入してベタイン構造体を得る。

【0071】

【化5】

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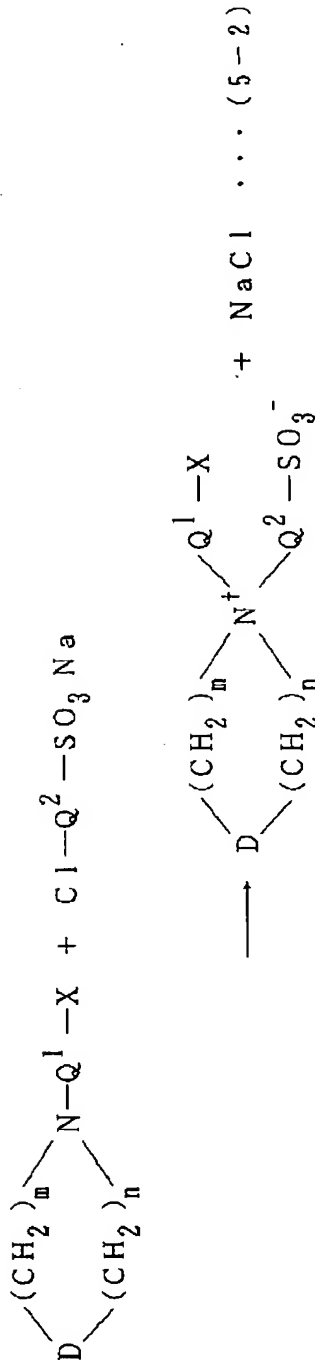
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【0072】

40 【化6】

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【0073】なお、本実施の形態においては、上記基本構造Xで表される水溶性染料に対してベタイン構造を導入することを、「ベタイン化」と表現する場合がある。また、ベタイン構造が導入された水溶性染料を、「(水溶性染料の名称)ベタイン化誘導体」または「(水溶性染料の名称)誘導体」と表現する(たとえば、「アシッドイエロー23ベタイン化誘導体」または、単に「アシッドイエロー23誘導体」と表現する)。

【0074】また、分子内塩を形成する上記ベタインは、通常は、本発明で用いられるベタイン構造のように、水溶液中で1つの両性イオンとして存在するもので

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あるが、水溶液中でカチオン・アニオンに分離してしまうものをベタインに含める場合もある。ここで、後者のように、水溶液中でカチオン・アニオンに分離してしまうものを用いてインクを調製すると、従来のインクと同様、事実上、該インクの組成中にカチオンが存在することになり、保存性の低下やコグーションの発生を招来することになるので好ましくない。

【0075】本発明にかかるカラーインクに必須成分として含まれているカチオン界面活性剤としては、水性溶媒中でイオンに解離して陽イオン(カチオン)となる部分が界面活性を示す物質であれば特に限定されるものではない。したがって、インクジェット用インクに使用できることが公知となっているカチオン界面活性剤は何れも本発明に適用することができる。

【0076】具体的には、たとえば、アミン塩、第4級アンモニウム塩、スルホニウム塩、ホスホニウム塩、カルボキシベタイン型、アミノカルボン酸塩、レシチン、サバミンA(チバガイギー製)、アーコベルG(アーノルドホフマン製)などを挙げることができる。上記の中でも、アミン塩および第4級アンモニウム塩が好ましく、特にアミン類の酢酸塩(アミン酢酸塩)や、第4級アンモニウムの酢酸塩または塩化物塩がより好ましい。

【0077】アミン類の酢酸塩の具体例としては、たとえば、最も長い疎水基が、炭素数12~18の範囲内のアルキル基であって、第1級アミン、第2級アミン、第3級アミン、およびそれらの混合物からなる群から選ばれるアミン類の酢酸塩などが好ましく挙げられる。このようなアミン類の酢酸塩としては、たとえばラウリルアミン酢酸塩などが挙げられる。

【0078】上記疎水基の炭素数が11以下となると、疎水性が低下して親水性となりやすい。一方、炭素数が19以上となると、疎水性が向上しすぎる。すなわち、上記疎水基の炭素数が12~18の範囲内から外れると、カチオン界面活性剤としての親水基と疎水基とのバランスが崩れてしまい、良好な界面活性効果(すなわち、後述する表面張力の調整効果)を発揮することができなくなるので好ましくない。

【0079】また、第4級アンモニウム塩の具体例としては、たとえば、ポリプロポキシ第4級アンモニウムアセテート類やポリプロポキシ第4級アンモニウムクロリド類などのポリプロポキシ第4級アンモニウム塩が好ましく用いられる。これらポリプロポキシ第4級アンモニウム塩は、何れもWITCO CorporationのEmcolシリーズなどとして市販されている。

【0080】上記カチオン界面活性剤と結合させることのできる対イオンの例としては、酢酸イオン、ギ酸イオン、塩化物イオン、グルコン酸イオン、コハク酸イオン、酒石酸イオン、グルタル酸イオン、マロン酸イオン、カルボン酸イオン、フマル酸イオン、リンゴ酸イオン、セバシン酸イオン、アジピン酸イオン、ステアリン



酸イオン、オレイン酸イオン、ラウリン酸イオン、安息香酸イオン、およびクエン酸イオンなどが挙げられる。中でも、上述したように、酢酸イオンや塩化物イオンが好ましく、酢酸イオンがより一層好ましい。

【0081】上記カチオン界面活性剤は、カラーインクの表面張力を調整するために添加されるものである。その具体的な含有量としては、該カラーインク中に、約0.5～5重量%の範囲内の濃度で存在しており、約3重量%の濃度となっていることがより好ましい。この範囲内でカチオン界面活性剤が含まれていることによって、サーマルジェットのヘッドにおけるオリフィスや被記録材（紙）上での濡れ性を良好に調整することが可能になる。

【0082】上記カチオン界面活性剤の含有量が約0.5重量%未満であれば、十分な表面張力の調整効果が得られないため好ましくない。一方、約5重量%を超えると、添加量に見合った表面張力の調整効果が得られない上に、粘性などが高くなってしまい、カラーインクとしての機能が低下するため好ましくない。

【0083】上記ベタイン構造を有する水溶性染料とカチオン界面活性剤とを含んでなる、本発明にかかるカラーインクは、酸性を示すものであり、具体的には、pHが4以上7未満の範囲内（カラーインクのpHをpH<sub>Cl</sub>とすると、 $4 \leq \text{pH}_{\text{Cl}} < 7$ ）が好ましく、pHが6以上7未満の範囲内（ $6 \leq \text{pH}_{\text{Cl}} < 7$ ）がより好ましい。すなわち、上記カラーインクは弱酸性を示すことがより好ましい。上記カチオン界面活性剤の添加によって、本発明にかかるカラーインクは弱酸性を示すことになるが、特に、カチオン界面活性剤としてアミン類の酢酸塩や第4級アンモニウム塩を用いれば、pHを6以上7未満のより好ましい範囲内に調整することができる。

【0084】なお、インクを酸性に調整するためにpH調整剤（緩衝剤／バッファー）を添加してもよい。ただし、本発明にかかるカラーインクでは、コゲーションの発生を回避する必要から、pH調整剤としては金属塩を含むものは用いることができない。

【0085】本発明にかかるカラーインクに含まれる水性溶媒としては、少なくとも水を含み、さらに水に可溶性他の溶媒を含んでなるものである。上記水としては、コゲーションを引き起こすような無機イオンが含まれておらず、一般的にインク用として用いられている程度の純度を有するものであれば特に限定されるものではないが、好ましくは、イオン交換水（脱イオン水）が用いられる。

【0086】カラーインク中における水の含有量としては、カラーインク全重量を100重量%とすると、10～90重量%の範囲内であり、30～80重量%の範囲内であることが好ましく、50～95重量%の範囲内であることがより好ましい。

【0087】上記水に可溶性他の溶媒としては、カラー

インクにおける各種作用、すなわちインクの乾燥や、発色、あるいは、本発明におけるコゲーションやカラーブリードの発生の抑制といった作用を阻害するものでなければ特に限定されるものではない。

【0088】上記他の溶媒としては、具体的には、たとえば、メタノール、エタノール、n-プロパノール、iso-プロパノール（2-プロパノール）、n-ブタノール、sec-ブタノール、tert-ブタノール、iso-ブタノール、n-ペンタノールなどの炭素数1～5のアルキルアルコール類；ジメチルホルムアミド、ジメチルアセトアミドなどのアミド類；アセトン、ジアセトンアルコールなどのケトンまたはケトアルコール類；テトラヒドロフラン、ジオキサンなどのエーテル類；ポリエチレングリコール、ポリプロピレングリコールなどのオキシプロピレン共重合体（ポリアルキレングリコール類）；ポリエチレンイミン；エチレングリコール、プロピレングリコール、ブチレングリコール、トリメチレングリコール、トリエチレングリコール、1, 2, 6-ヘキサントリオール、チオグリコール、ヘキシレングリコール、ジエチレングリコール、テトラエチレングリコール、ジプロピレングリコール、トリプロピレングリコール、1, 5-ペンタンジオール、グリセリンなどの多価アルコール類；エチレングリコールモノメチルエーテル、エチレングリコールモノエチルエーテル、ジエチレングリコールモノメチルエーテル、ジエチレングリコールモノエチルエーテル、ジエチレングリコールモノブチルエーテル、トリエチレングリコールモノメチルエーテル、トリエチレングリコールモノエチルエーテルなどの多価アルコールの低級モノアルキルエーテル類；トリエチレングリコールジメチルエーテル、トリエチレングリコールジエチルエーテル、テトラエチレングリコールジメチルエーテル、テトラエチレングリコールジエチルエーテルなどの多価アルコールの低級ジアルキルエーテル類；トリメチロールプロパン；モノエタノールアミン、ジエタノールアミン、トリエタノールアミン、2-ピロリドン、N-メチル-2-ピロリドン、1, 3-ジメチル-2-イミダゾリジノン、スルホランなどの有機アミン類；尿素；などといった、各種の水溶性有機溶剤が挙げられる。上記水溶性有機溶剤は、単独で用いてもよく、2種類以上の混合物としても用いてもよい。

【0089】上記水溶性有機溶剤の中でも、特に、iso-プロパノール（2-プロパノール）などの一価のアルコール、ジエチレングリコールや1, 5-ペンタンジオールなどの多価アルコール、トリエチレングリコールモノメチル（またはエチル）エーテルやジエチレングリコールモノブチルエーテルなどの多価アルコールの低級アルキルエーテル、トリメチロールプロパンなどが好ましい。一価のアルコールは、低沸点であるため、画像形成時に、カラーインクの乾燥時間を短縮する効果が得られる。また、多価アルコールや多価アルコールの低級アル

キルエーテルは高沸点であるため、カラーインクの望ましくない乾燥を抑制する湿潤剤として機能する。

【0090】本発明にかかるカラーインク中に含まれる上記水溶性有機溶剤の含有量は、特に限定されないが、カラーインク全重量を100重量%とした場合に、3～50重量%の範囲内が好ましく、3～40重量%の範囲内がより好ましい。

【0091】また、上記水溶性有機溶剤を低沸点のものと高沸点のものに分けて添加する場合には、低沸点有機溶剤の場合は、カラーインクを100重量%とした場合に、0.5～10重量%の範囲内が好ましく、1.5～6重量%の範囲内がより好ましい。また、高沸点有機溶剤の場合は、カラーインクを100重量%とした場合に、0.5～40重量%の範囲内が好ましく、2～20重量%の範囲内がより好ましい。

【0092】なお、上述した水溶性有機溶剤の含有量の好ましい範囲は、何れも、各水溶性有機溶剤を単独で用いた場合も2種類以上の混合物として用いた場合も含むものとする。すなわち、上記好ましい範囲とは、水溶性有機溶剤のトータルの含有量としての好ましい範囲である。

【0093】また、本発明にかかるカラーインクは、所望の物性値を得るために、上述した成分の他に、必要に応じて、消泡剤、防腐剤、防カビ剤などを添付することができ、さらには、その他の市販の水溶性染料なども添加することができる。これら消泡剤、防腐剤、防カビ剤などの具体例や添加量については、カラーインクの諸特性に悪影響を及ぼさない限り特に限定されるものではなく、従来公知の技術を好適に用いることができる。

【0094】本発明にかかるインクジェット用インクセットにおいては、上記各成分を含むカラーインクに加えて、水性溶媒中に黒色顔料を含む組成を必須とし、かつアルカリ性を示すブラックインクを含んでいる。

【0095】上記ブラックインクに含まれる黒色顔料としては、一般にブラックインク用に用いられるカーボンブラックなどを挙げることができ、特に限定されるものではないが、中でも、黒色顔料の表面にカルボキシル基が修飾されることによって、水溶液中でアニオン性に帯電するアニオン顔料が特に好ましい。

【0096】このアニオン顔料の具体的な例としては、カーボンブラックの表面に $\text{COONa}$ （カルボキシル基のナトリウム塩）を導入してアニオン性に帯電したカーボンブラックを得る方法が挙げられる。具体的には、たとえば、市販の酸性カーボンブラックを水によく混合して分散させた後、これに次亜塩素酸ナトリウムを滴下して加熱し、その後、得られたスラリーを濾過・水洗して顔料ウェットケーキを得て、さらに、これを水に再分散させて逆浸透膜で脱塩し、さらに、この顔料分散液を濃縮するという方法が挙げられるが、特に限定されるものではない。

【0097】さらに、市販の自己分散型カーボンブラックを、アニオン顔料として用いることも可能である。たとえば、カルボキシル基（ $\text{COO}^-$ ）が直接結合してアニオン性に帯電した自己分散型カーボンブラック「キャボジェット」（商品名、キャボット製）などが挙げられる。

【0098】上記ブラックインクには、黒色顔料を分散させるための分散剤が含まれていることが非常に好ましい。特に、自己分散型でないようなカーボンブラックを用いる場合には、該カーボンブラックの沈殿を回避して保存性を向上させる点から、分散剤が添加されることが非常に好ましい。

【0099】この分散剤としては、具体的には、カルボキシル基を有する各種樹脂を挙げることができる。このようなカルボキシル基を有する各種樹脂が分散剤として添加されていると、ブラックインクはアルカリ性を示し、黒色顔料、特にアニオン顔料は、この条件下で安定な溶液（分散液／懸濁液）となる。その結果、長期間放置しても顔料が沈殿したり凝固したりすることが抑制され、優れた保存性を得ることができる。

【0100】上記カルボキシル基を有する各種樹脂としては、たとえば、スチレン-アクリル酸共重合体、スチレン-アクリル酸-アクリル酸アルキルエステル共重合体、スチレン-マレイン酸共重合体、スチレン-マレイン酸-アクリル酸アルキルエステル共重合体、スチレン-メタクリル酸共重合体、スチレン-メタクリル酸-アクリル酸アルキルエステル共重合体、スチレン-マレイン酸-ハーフエステル共重合体、ビニルナフタレン-アクリル酸共重合体、ビニルナフタレン-マレイン酸共重合体、あるいはこれらの塩などが挙げられる。中でも、スチレン-アクリル系樹脂が好ましく、スチレン-アクリル酸共重合体が特に好ましい。

【0101】上記各種の樹脂は、ブラックインク全体を100重量%とした場合に、0.1～5重量%の範囲内で含有されていることが好ましく、0.3～2重量%の範囲内で含有されることがより好ましい。

【0102】なお、上記各種の樹脂には、後述する結着剤としても使用可能なものも含まれる。その場合には、ブラックインクに添加される成分数が少なくなるので、ブラックインクの調製を簡素化することができる。

【0103】また、上記分散剤としては、他に、樹脂エマルジョンが挙げられる。ここで言う樹脂エマルジョンとは、連続相が水であり、分散相が次のような樹脂成分であるエマルジョンを意味する。

【0104】上記樹脂エマルジョンにおける分散相の樹脂成分としては、アクリル系樹脂、酢酸ビニル系樹脂、スチレン-ブタジエン樹脂、塩化ビニル系樹脂、アクリル-スチレン系樹脂、ブタジエン系樹脂、スチレン系樹脂、架橋アクリル樹脂、架橋スチレン樹脂、ベンゾグアナミン樹脂、フェノール樹脂、シリコーン樹脂、エポキ

シ樹脂などが挙げられる。

【0105】上記樹脂エマルジョンは、樹脂モノマーを、状況によって界面活性剤とともに水中で分散重合（乳化重合）することによって得ることができる。たとえば、アクリル系樹脂またはスチレン-アクリル系樹脂のエマルジョンは、（メタ）アクリル酸エステル、または（メタ）アクリル酸エステルおよびスチレンを、界面活性剤とともに水中で分散重合させることによって得られる。

【0106】上記分散相成分としての樹脂と水との割合は、樹脂100重量部に対して水60～400重量部、好ましくは100～200重量部の範囲内が適当である。

【0107】また、市販の樹脂エマルジョンを使用することも可能である。市販の樹脂エマルジョンとしては、たとえば、マイクロジェルE-1002、E-5002（スチレン-アクリル系樹脂エマルジョン、日本ペイント株式会社製）、ボンコート4001（アクリル系樹脂エマルジョン、大日本インキ化学工業株式会社製）、ボンコート5454（スチレン-アクリル系樹脂エマルジョン、大日本インキ化学工業株式会社製）、SAE-1014（スチレン-アクリル系樹脂エマルジョン、日本ゼオン株式会社製）、サイビノールSK-200（アクリル系樹脂エマルジョン、サイデン化学株式会社製）、などが挙げられる。

【0108】本発明では、上記樹脂エマルジョンは、ブラックインクを100重量%とすると、0.1～40重量%の範囲内で含まれていることが好ましく、1～25重量%の範囲内で含まれていることがより好ましい。

【0109】また、本発明における分散剤としては、上記カルボキシル基を有する樹脂と、上記樹脂エマルジョンとの両方が含まれていてもよい。さらに、黒色顔料が分散性の高いアニオン顔料である場合などには、分散剤は必ずしも含まれている必要はない。

【0110】さらに、上記ブラックインクには、画像形成時に被記録材上に黒色顔料を定着させる結着剤が含まれていてもよい。この結着剤としては、たとえば、ポリウレタン樹脂、デンプン、ゼラチン、ラテックス、カゼイン、アラビアゴム、アルギン酸ナトリウム、ポリアクリルアミドなどの水溶性高分子；メチルセルロース、カルボキシセルロース、ヒドロキシメチルセルロースなどのセルロース誘導体；ポリアクリル酸塩、ビニルナフタレン-アクリル酸共重合体、スチレン-マレイン酸共重合体およびその塩、 $\beta$ -ナフタレンスルホン酸ホルマリン縮合体のナトリウム塩、リン酸塩などのアニオン性（陰イオン性）高分子；ポリビニルアルコール、ポリビニルピロリドン、ポリエチレングリコールなどのノニオン性（非イオン性）高分子などが挙げられる。

【0111】上記結着剤の含有量は、ブラックインクを100重量%とした場合に、0.5～30重量%の範囲

内で含有されることが好ましい。0.5重量%未満であれば結着剤を添加することによる効果が得られない。一方、30重量%を超えると、添加量に見合った効果が得られない上に、粘性などが高くなってしまい、ブラックインクとしての機能が低下するため好ましくない。

【0112】上記ブラックインクに含まれる水性溶媒としては、前述したカラーインクと同様に、少なくとも水を含み、さらに水に可溶な他の溶媒を含んでなるものである。上記水としても他の溶媒としても、何れも前述したカラーインクの説明で例示した水溶性有機溶剤と同様であるため、その詳細な説明は省略する。

【0113】上記ブラックインクは、上述したようにアルカリ性を示すものであり、具体的には、pHが7を超え10以下となる範囲内（ブラックインクのpHをpH<sub>Bk</sub>とすると、 $7 < \text{pH}_{\text{Bk}} \leq 10$ ）が好ましく、pHが7を超え9以下となる範囲内（ $7 < \text{pH}_{\text{Bk}} \leq 9$ ）がより好ましい。すなわち、上記ブラックインクは弱アルカリ性を示すことがより好ましい。

【0114】ここで、上記ブラックインクには、前述した水溶性有機溶剤の中でも、たとえば2-ピロリドンなどの有機アミン類が含まれていることが非常に好ましい。この有機アミン類は、ブラックインクを弱アルカリ性に調整するpH調整剤（緩衝剤/バッファー）として機能するとともに、コゲーションは引き起こさないため、好ましく用いられる。また、その含有量は、ブラックインクを100重量%とした場合に、0.001～10重量%の範囲内で含有されることが好ましい。

【0115】また、本発明にかかるブラックインクは、所望の物性値を得るために、上述した成分の他に、必要に応じて、消泡剤、防腐剤、防カビ剤などを添付することができ、さらには、その他の市販の水溶性染料なども添加することができる。これら消泡剤、防腐剤、防カビ剤などの具体例や添加量については、ブラックインクの諸特性に悪影響を及ぼさない限り特に限定されるものではなく、従来公知の技術を好適に用いることができる。

【0116】本発明にかかるインクジェット用インクとしてのカラーインク、および該カラーインクと上記ブラックインクを含む、本発明にかかるインクセットは、従来公知の各種インクジェットプリンタに広く適用することができる。

【0117】上記インクジェットプリンタの代表的な方式としては、ノズル内のインクをピエゾ素子の物理的変形によって吐出するピエゾジェット方式や、ノズル内のインクに熱を加えて発生する気泡によって吐出するサーマルジェット方式が挙げられる。本発明にかかるインクセットは、上記何れの方式にも好適に用いることができるが、中でも、インクを加熱することによってコゲーションが発生し易いサーマルジェット方式に特に好ましく用いられる。

【0118】上記インクジェット記録方式においては、

上記ブラックインクとカラーインクとが、ヘッドのノズルからそれぞれ別個に吐出され、被記録材としてのたとえば紙上で画像を形成することによって互いに接触する。

【0119】ここで、従来では、特にブラックと、他の色との境界となる部分では、各インク同士が拡散したり移動したりして各色の境界線が不明確となる現象、すなわちカラーブリードが発生する。その結果、特に、ブラックの画像の境界がにじんだりぼやけたりして、非常に画像品位を低下させることになっていた。

【0120】また、インクの組成上の問題から、ノズルのヒータ部分にインク成分が付着するなどしてコグーションを生じたり、画像形成の頻度が小さく、画像形成動作の間の時間が長いような場合には、インクの染料や顔料が凝固したり沈殿したりしてノズルが詰まってしまう、保存性も低下するという問題点を招来していた。

【0121】これに対して本発明においては、まず、ヘッド内では、ブラックインクは、アルカリ性条件下で安定して黒色顔料を分散（懸濁）した状態にある一方、カラーインクは、酸性条件下で、ベタイン構造を有する水溶性染料が安定した状態にある。しかも、これら各インクには、金属塩やゲル化に関わる成分などがほとんど含まれていない。そのため、ノズルで加熱されてもコグーションを生じず、また、画像形成の頻度が小さく、画像形成動作の間の時間が長いような場合であっても、黒色顔料や水溶性染料が凝固したり沈殿することがない。

【0122】さらに、ブラックインクとその他のカラーインクとが被記録材上で会合すると、アルカリ性のブラックインクと酸性のカラーインクとが酸-アルカリ反応を起して、ブラックインクのイオン電荷のバランスが低下する。ブラックインクでは、イオンの電荷バランスが良好な状態では、黒色顔料が均一に分散しているが、そのバランスが低下すると、非常に容易に沈殿（または凝固）し易くなるため、黒色顔料は被記録材上で容易かつ迅速に沈殿する。その結果、黒色顔料がカラーブリードを起こさずに定着することになって、カラーブリードを抑制することができる。

【0123】上記カラーブリードの抑制機構をより具体的に説明する。たとえば、ブラックインクが、黒色顔料としてアニオン顔料を、分散剤としてスチレン-アクリル系樹脂を含んでいるとして、カラーインクがベタイン構造の水溶性染料と、カチオン界面活性剤とを含んでいるとする。

【0124】これらがノズルから別々に吐出され、被記録剤上で会合すると、アニオン顔料を良好に分散させていた分散剤であるスチレン-アクリル系樹脂と、カラーインクのカチオン界面活性剤とが酸-アルカリ反応を起こす。すなわち、スチレン-アクリル系樹脂の末端にあるカルボキシル基と、カチオン界面活性剤において界面活性効果を示すカチオンとが反応し、この反応をドライ

ビングフォースとして、ブラックインク中のイオン電荷バランスが不安定になる。これによってアニオン顔料は容易に沈殿する一方、ブラックインク中で分散していた上記スチレン-アクリル系樹脂も容易に凝固する。

【0125】その結果、沈殿したアニオン顔料をスチレン-アクリル系樹脂が定着させることになり、ブラックインクが被記録材に浸透もせず、カラーインクとの間にカラーブリードを発生させることもなく、確実に固化・凝集する。

【0126】このように、本発明にかかるインクジェット記録方式では、アルカリ性のブラックインクと酸性のカラーインクとを用いることによって、被記録材上で酸-アルカリ反応をドライビングフォースとするブラックの定着反応を生じさせる。その結果、カラーブリードが確実に抑制される。

【0127】しかも、上記各インクには、金属塩やゲル化反応に関わるような成分が含まれていないため、特にサーマルジェット方式のインクジェットプリンタであってもコグーションを生じさせることがない。さらに、上記各インクは、カラーブリードを抑制させるために、本来ならインクとして不安定な状態である酸性またはアルカリ性を示している。しかしながら、水溶性染料をベタイン化するとともに、アニオン化および分散剤によって顔料を良好に分散させているため、長期間放置してもインク成分が凝固したり沈殿したりせず、ノズルが詰まり画像形成できないといった問題点も回避することができる。その結果、インクの保存性も非常に向上したものとなっている。

【0128】

【実施例】以下、実施例、および比較例に基づいて本発明をさらに詳細に説明するが、本発明はこれらに限定されるものではない。なお、以下の説明では、重量部を単に「部」と略記し、重量%も単に「%」と略記する。

【0129】また、カラーブリード、コグーション、および保存性については、下記の方法により評価した。

【0130】〔カラーブリード〕市販のサーマルヘッド方式のカラーインクジェットプリンタを用いて、PPC用紙に画像を形成した場合における、異なる色間でのにじみなどが発生して、各色の境界が不明確になっているか否かを目視にて確認した。このとき、全くににじみなどが発生せず、各色の境界が明確になっている場合を○、にじみなどが発生して、各色の境界が不明確となっている場合を×として評価した。

【0131】〔コグーション〕カラーブリードの評価と同様、サーマルジェット方式のカラーインクジェットプリンタを用いて、インクカートリッジの規定量まで各カラーインクを充填し、各カラーインクを全て画像形成で使い切る動作を二回繰り返した。この画像形成時点で、画像にかすれなどが発生していないかを目視にて確認した。その後、カートリッジを分解してサーマルヘッドの

ヒータ部分を目視にて確認した。

【0132】このとき、画像形成中にかすれなどの異常が確認されず、かつ、ヒータ部分が、画像形成を実施する前とほぼ同じで何ら異常な状態が見られない場合を○、画像形成中にかすれなどの異常が確認されたり、何らかの付着物などが見られたりした場合を×として評価した。

【0133】〔保存性〕カラーブリードおよびコゲーションの評価と同様、サーマルジェット方式のカラーインクジェットプリンタを用いて、インクカートリッジの規定量まで各カラーインクを充填し、常温で3カ月間そのままの状態に保管した。その後、該インクカートリッジを用いて、保管前と同様の通常の画像形成を実施した。そして、次の3点について評価を実施した。

#### 【0134】1. 画像形成動作

上記画像形成動作をカラーインクの保管前後で比較した。このとき、ヘッドからカラーインクが吐出できず画像形成できない場合を×、一応画像形成はできるものの、ある程度画像形成した後に形成された画像にかすれが見られる場合を△、保管前と何ら変わらず良好な画像形成ができた場合を◎として評価した。

#### 【0135】2. サーマルヘッドのヒータ

保管後の画像形成動作を終了した後に、コゲーションの評価と同様、カートリッジを分解してサーマルヘッドのヒータ部分を目視にて確認した。このとき、ヒータ部分が、画像形成を実施する前とほぼ同じで何ら異常な状態が見られない場合を○、何らかの付着物などが見られた場合を×として評価した。

#### 【0136】3. インクの状態

保管後の画像形成動作を終了した後に、カラーインクそのものの状態を目視で確認した。このとき、保管前と変わらず凝固や沈殿が生じていない場合を○、何らかの凝集物が発生している場合を×として評価した。

【0137】上記三つの評価を総合することによって、カラーインクの保存性を評価した。すなわち、上記三つの全ての評価が○である場合を○、上記三つの評価のうち一つでも△がある場合を△、上記三つの評価のうち一つでも×がある場合を×として評価した。

【0138】〔実施例1〕本実施例においては、本発明にかかるインクセットとして、表1に示す組成のブラックインクおよびシアン、マゼンタ、およびイエローの各カラーインクを調製し、これらインクセットを用いて画像形成を行った。

【0139】すなわち、黒色顔料としてカーボンブラックMA7（三菱化学製）を、分散剤としてスチレンーア

クリル酸共重合体を、結着剤としてポリウレタンエマルジョンを用いるとともに、溶媒として純水（イオン交換水）と、他の水溶性有機溶剤として2-ピロリドン、ジエチレングリコールモノブチルエーテル、トリメチロールプロパン、および2-プロパノールとを用いて、これらを表1に示す含有量となるように配合し、本発明にかかるブラックインク（1）を調製した。このブラックインク（1）のpHは約8であり、弱アルカリ性を示した。

【0140】次に、カラーインクの調製について説明すると、まずシアンのカラーインクの調製に当たっては、水溶性染料として、ダイレクトブルー199（ダイワ化成製）およびアシッドブルー9（ダイワ化成製）を用い、これら各染料に対して従来公知の方法（前記実施の形態参照）にてベタイン構造を導入して、本発明に用いられるベタイン構造を有する水溶性染料としての、ダイレクトブルー199ベタイン化誘導体、およびアシッドブルー9ベタイン化誘導体を得た。

【0141】同様にマゼンタのカラーインクの調製に当たっては、水溶性染料として、アシッドレッド52（ダイワ化成製）およびリアクティブレッド180（クラリアント製）を用い、これら各染料に対して従来公知の方法にてベタイン構造を導入して、本発明に用いられるベタイン構造を有する水溶性染料としての、アシッドレッド52ベタイン化誘導体、およびリアクティブレッド180ベタイン化誘導体を得た。

【0142】同様にイエローのカラーインクの調製に当たっては、水溶性染料として、アシッドイエロー23（ダイワ化成製）を用い、従来公知の方法にてベタイン構造を導入して、本発明に用いられるベタイン構造を有する水溶性染料としてのアシッドイエロー23ベタイン化誘導体を得た。

【0143】上記各ベタイン化誘導体に加えて、カチオン界面活性剤としてラウリルアミン酢酸塩を用い、さらに溶媒として純水（イオン交換水）と、他の水溶性有機溶剤として2-ピロリドン、トリメチロールプロパン、および1,5-ペンタンジオールまたはジエチレングリコールとを用いて、これらを表2に示す含有量となるように配合して、シアン、マゼンタ、およびイエローの各カラーインク（1）を調製した。これら各カラーインク（1）のpHは約5～6であり、何れも弱酸性を示した。

#### 【0144】

#### 【表1】

		成 分 名	含有量 (重量%)
黒色顔料		カーボンブラックMA7	5
分散剤		スチレン-アクリル酸共重合体	1
結着剤		ポリウレタンエマルジョン	2
水 性 溶 媒	水溶性有機溶剤	2-ピロリドン	6
		ジエチレングリコールモノブチルエーテル	6
		トリメチロールプロパン	6
		2-プロパノール	2
	水	純 水	(残 量)
計		ブラックインク(1)	100

【0145】

【表2】

	シアインク (1)		マゼンタインク (1)		イエローインク (1)	
	成分名	含有量 (重量%)	成分名	含有量 (重量%)	成分名	含有量 (重量%)
水性染料の ベタイン化 誘導体	ダイレクトブル 199誘導体	2	アシッドレッド52 誘導体	0.5	アシッドイエロー 23誘導体	2.5
	アシッドブルー9 誘導体	1	リアクティブレッド 180誘導体	2.5		
カチオン 界面活性剤	ラウリルアミン酢酸 塩	2	ラウリルアミン酢酸 塩	2	ラウリルアミン酢酸 塩	3
水性 有機溶剤	トリメチロールプロ パン	6	トリメチロールプロ パン	6	トリメチロールプロ パン	7
	2-ピロリドン	6	2-ピロリドン	6	2-ピロリドン	4
	1,5-ペンタンジオ ール	7	1,5-ペンタンジオ ール	7	ジエチレングリコ ール	4
水	純水	(残量)	純水	(残量)	純水	(残量)
計		100		100		100

【0146】なお、上記表2、および後記の表4および表5においては、水性染料のベタイン化誘導体を、単に、「(水性染料の名称)誘導体」と略記している。また、後記の表6および表7に記載している水性染料には、「誘導体」という記載がないが、これは、ベタイン構造を導入しない元のままの水性染料であることを示しており、上記ベタイン化誘導体とは異なるものである。

【0147】上記ブラックインク(1)を、上述したサーマルヘッド方式のカラーインクジェットプリンタにおけるヘッド一体型のインクカートリッジに充填した。また、上記シアン、マゼンタ、イエローの各カラーインク

(1)を、上記カラーインクジェットプリンタにおける3色一体型・ヘッド一体型のインクカートリッジに規定量となるまで充填した。

【0148】上記インクカートリッジを用いて、被記録材として、一般に用いられているPPC用紙を用いて、上記各カラーインク(1)を完全に消費するまで画像形成を行った。さらにその後、上記各カラーインク(1)をインクカートリッジに規定量となるまで充填し、再び各カラーインク(1)を完全に消費するまで画像形成を行った。

【0149】その後、用紙上に形成された画像を目視にて確認し、カラーブリードについて評価した。また、画

像形成終了後、インクカートリッジを分解してインクヘッドのヒーター部分を目視にて観察し、コゲーションについて評価した。評価結果を後記の表8に示す。

【0150】さらに、上記各カラーインク（1）をインクカートリッジに充填したままの状態では3カ月間保管した後に、上記と同様にして画像形成を行った。この保管後の画像形成動作および形成された画像を、保管前と比較することによって、保存性について評価した。評価結果を後記の表8に示す。

【0151】〔実施例2〕本実施例においては、本発明にかかるインクセットとして、表3に示す組成のブラックインクおよびシアン、マゼンタ、およびイエローの各カラーインクを調製し、これらインクセットを用いて画像形成を行った。

【0152】市販の自己分散型カーボンブラック「キャボジェット」（商品名、キャボット製）を黒色顔料として用い、結着剤としてポリウレタンエマルジョンを用いるとともに、溶媒として純水（イオン交換水）と、他の水溶性有機溶剤として2-ピロリドン、ジエチレングリコールモノブチルエーテル、ポリエチレンイミン、および2-プロパノールとを用いて、これらを表3に示す含有量となるように配合し、本発明にかかるブラックインク（2）を調製した。このブラックインク（2）のpHは約8であり、弱アルカリ性を示した。

【0153】次に、カラーインクの調製について説明すると、まずシアンのカラーインクの調製に当たっては、水溶性染料として、アシッドブルー7（ダイワ化成製）を用い、従来公知の方法にてベタイン構造を導入して、

本発明に用いられるベタイン構造を有する水溶性染料としての、アシッドブルー7ベタイン化誘導体を得た。

【0154】同様にマゼンタのカラーインクの調製に当たっては、水溶性染料として、アシッドレッド52（ダイワ化成製）およびリアクティブレッド58（ダイワ化成製）を用い、これら各染料に対してそれぞれ従来公知の方法にてベタイン構造を導入して、本発明に用いられるベタイン構造を有する水溶性染料としての、アシッドレッド52ベタイン化誘導体、およびリアクティブレッド58ベタイン化誘導体を得た。

【0155】同様にイエローのカラーインクの調製に当たっては、水溶性染料として、アシッドイエロー23（ダイワ化成製）を用い、従来公知の方法にてベタイン構造を導入して、本発明に用いられるベタイン構造を有する水溶性染料としてのアシッドイエロー23ベタイン化誘導体を得た。

【0156】上記各ベタイン化誘導体に加えて、カチオン界面活性剤としてラウリルアミン酢酸塩を用い、さらに溶媒として純水（イオン交換水）と、他の水溶性有機溶剤としてポリエチレンイミン、2-ピロリドン、および1, 5-ペンタンジオールまたはジエチレングリコールとを用いて、これらを表4に示す含有量となるように配合して、シアン、マゼンタ、およびイエローの各カラーインク（2）を調製した。これら各カラーインク（2）のpHは約5～6であり、何れも弱酸性を示した。

【0157】

【表3】

		成分名	含有量 (重量%)
黒色顔料		キャボジェット	5
分散剤		—	—
結着剤		ポリウレタンエマルジョン	2
水性 溶 媒	水溶性有機溶剤	2-ピロリドン	6
		ジエチレングリコールモノブチルエーテル	6
		ポリエチレンイミン	6
		2-プロパノール	2
	水	純水	(残量)
計		ブラックインク（2）	100

【0158】

【表4】



	シアンインク (2)		マゼンタインク (2)		イエローインク (2)	
	成分名	含有量 (重量%)	成分名	含有量 (重量%)	成分名	含有量 (重量%)
水溶性染料の ベタイン化 誘導体	アシッドブルー-7 誘導体	3	アシッドレッド52 誘導体	0.5	アシッドイエロー 23誘導体	2.5
			リアクティブレッド 58誘導体	2.5		
カチオン 界面活性剤	ラウリルアミン酢酸 塩	2	ラウリルアミン酢酸 塩	2	ラウリルアミン酢酸 塩	3
水性 有機溶媒	ポリエチレニンミン	6	ポリエチレニンミン	6	ポリエチレニンミン	7
	2-ピロリドン	6	2-ピロリドン	6	2-ピロリドン	4
	1,5-ペンタンジオ ール	7	1,5-ペンタンジオ ール	7	ジエチレングリコ ール	4
水	純水	(残 量)	純水	(残 量)	純水	(残 量)
計		100		100		100

【0159】上記ブラックインク (2) および上記シ  
アン、マゼンタ、イエローの各カラーインク (2) を、上  
述したサーマルヘッド方式のカラーインクジェットプリン  
タにおけるインクカートリッジに実施例1と同様にし  
て充填した。そして、実施例1と同様の画像形成を行っ  
て、カラーブリード、コゲーション、および保存性につ  
いて評価した。評価結果を後記の表8に示す。

【0160】〔比較例1〕前記実施例1と同様にし  
てブラックインク (1) を調製 (表1参照) した。また、本  
発明にかかるカラーインクに必須の成分である、カチオ

ン界面活性剤を用いず、アニオン界面活性剤としてラ  
ウリル硫酸ナトリウムを用いた以外は、前記実施例1と  
同様にし、シアン、マゼンタ、およびイエローの各比  
較カラーインク (1) を調製した。これら各比較カラー  
インク (1) のpHは約8~9であり、何れも弱アルカ  
リ性を示した。各比較カラーインク (1) における各成  
分の含有量を表5に示す。

【0161】

【表5】

	比較シアインク (1)		比較マゼンタインク (1)		比較イエローインク (1)	
	成分名	含有量 (重量%)	成分名	含有量 (重量%)	成分名	含有量 (重量%)
水溶性染料の ベタイン化 誘導体	ダイレクトブルー 199誘導体	2	アシッドレッド52 誘導体	0.5	アシッドイエロー 23誘導体	2.5
	アシッドブルー9 誘導体	1	リアクティブレッド 180誘導体	2.5		
アニオン 界面活性剤	ラウリル硫酸ナトリ ウム	2	ラウリル硫酸ナトリ ウム	2	ラウリル硫酸ナトリ ウム	3
水性溶媒	トリメチロールプロ パン	6	トリメチロールプロ パン	6	トリメチロールプロ パン	7
	2-ピロリドン	6	2-ピロリドン	6	2-ピロリドン	4
	1,5-ペンタンジオ ール	7	1,5-ペンタンジオ ール	7	ジエチレングリコー ル	4
水	純水	(残量)	純水	(残量)	純水	(残量)
計		100		100		100

【0162】上記ブラックインク (1) および比較カラーインク (1) を用いて、前記実施例 1 と同様にして画像形成を行って、カラーブリード、コゲーション、および保存性について評価した。また、評価結果を後記の表 8 に示す。

【0163】〔比較例 2〕前記実施例 1 と同様にしてブラックインク (1) を調製 (表 1 参照) した。また、本発明にかかるカラーインクに必須の成分である、ベタイン構造を有する水溶性染料を用いない以外は、前記実施例 1 と同様にして、シアン、マゼンタ、およびイエロー

の各比較カラーインク (2) を調製した。これら各比較カラーインク (2) の pH は約 5~6 であり、何れも弱酸性を示した。各比較カラーインク (2) における各成分の含有量を表 6 に示す。なお、表 6 および後記の表 7 に示す各水溶性染料は、前述した通り、前記実施例 1 におけるベタイン構造を導入する前の各水溶性染料と同一のものである。

【0164】

【表 6】

	比較シアインク (2)		比較マゼンタインク (2)		比較イエローインク (2)	
	成分名	含有量 (重量%)	成分名	含有量 (重量%)	成分名	含有量 (重量%)
水溶性染料	ダイレクトブルー 199	2	アシッドレッド52	0.5	アシッドイエロー 23	2.5
	アシッドブルー9	1	リアクティブレッド 180	2.5		
カチオン 界面活性剤	ラウリルアミン酢酸 塩	2	ラウリルアミン酢酸 塩	2	ラウリルアミン酢酸 塩	3
水性溶媒	トリメチロールプロ パン	6	トリメチロールプロ パン	6	トリメチロールプロ パン	7
	2-ピロリドン	6	2-ピロリドン	6	2-ピロリドン	4
水	1,5-ペンタンジオ ール	7	1,5-ペンタンジオ ール	7	ジエチレングリコー ル	4
	純水	(残量)	純水	(残量)	純水	(残量)
計		100		100		100

【0165】上記ブラックインク (1) および比較カラーインク (2) を用いて、前記実施例 1 と同様にして画像形成を行って、カラーブリード、コゲーション、および保存性について評価した。また、評価結果を後記の表 8 に示す。

【0166】〔比較例 3〕前記実施例 1 と同様にしてブラックインク (1) を調製 (表 1 参照) した。また、コゲーションを導くために本発明のカラーインクには添加しない成分である、多価金属塩 (カチオン塩) としての

硝酸マグネシウムまたは硝酸カルシウムを用いた以外は、前記実施例 1 と同様にして、シアン、マゼンタ、およびイエローの各比較カラーインク (3) を調製した。これら各比較カラーインク (3) の pH は約 6~7 であり、何れも弱酸性を示した。各比較カラーインク (3) における各成分の含有量を表 7 に示す。

【0167】

【表 7】

	比較シアインク (3)		比較マゼンタインク (3)		比較イエローインク (3)	
	成分名	含有量 (重量%)	成分名	含有量 (重量%)	成分名	含有量 (重量%)
水溶性染料	ダイレクトブルー 199	2	アシッドレッド52	0.5	アシッドイエロー 23	2.5
	アシッドブルー9	1	リアクティブレッド 180	2.5		
ノニオン 界面活性剤	アセチレンジグリコー ル	2	アセチレンジグリコー ル	2	アセチレンジグリコー ル	3
多価金属塩	硝酸マグネシウム	3	硝酸マグネシウム	3	硝酸カルシウム	5
水性 溶解媒	トリメチロールプロ パン	6	トリメチロールプロ パン	6	トリメチロールプロ パン	7
	2-ピロリドン	6	2-ピロリドン	6	2-ピロリドン	4
	1,5-ペンタンジオ ール	7	1,5-ペンタンジオ ール	7	ジエチレンジグリコー ール	4
	純水	(残 量)	純水	(残 量)	純水	(残 量)
計		100		100		100

【0168】上記ブラックインク (1) および比較カラーインク (3) を用いて、前記実施例1と同様にして画像形成を行って、カラーブリード、コゲーション、および保存性について評価した。また、評価結果を下記の表

8に示す。

【0169】

【表8】

		実施例 1	実施例 2	比較例 1	比較例 2	比較例 3
ブラック インク	種類	(1)	(2)	(1)	(1)	(1)
	pH	8	8	8	8	8
カラー インク	種類	(1)	(2)	比較(1)	比較(2)	比較(3)
	pH	5~6	5~6	8~9	5~6	6~7
	水溶性染料 のベタイン 化の有無	あり	あり	あり	なし	なし
	界面活性剤	カチオン	カチオン	アニオン	カチオン	ノニオン
	多価金属塩	なし	なし	なし	なし	あり
カラーブリード		○	○	×	○	○
コゲーション		○	○	○	×	×
保管 後	1. 動作	○	○	○	×	△
	2. ヒータ	○	○	○	×	×
	3. インク	○	○	○	×	○
保存性		○	○	○	×	×

【0170】表8の結果から明らかなように、本発明にかかるインクジェット用インクセットを用いた場合は、カラーブリードの防止、コゲーションの防止、保存性の向上の全てを達成することが可能であった（実施例 1・2）。しかしながら、水溶性染料にベタイン構造を導入しなければ、保存性が低下する上に、コゲーションの発生も防止できなかった（比較例 2・3）。特に、カチオン塩を用いると、保存性が非常に悪化した（比較例 2）。

【0171】一方、水溶性染料にベタイン構造を導入すれば、コゲーションの防止と保存性の向上とを十分に達成することができるが（実施例 1・2、比較例 1）、カチオン界面活性剤を用いなければ、カラーブリードの発生を防止できず、画質が大幅に劣化した（比較例 1）。

【0172】このように、本発明にかかるインクジェット用インクでは、水性溶媒中に、ベタイン構造を有する水溶性染料と、カチオン界面活性剤とを含んでなるため、カラーブリードの防止、コゲーションの防止、保存性の向上の全てを達成することができる優れたインクとすることができる。

【0173】

【発明の効果】以上のように、本発明にかかるインクジェット用インクは、水性溶媒中に、ベタイン構造を有する水溶性染料と、カチオン界面活性剤とを含んでなる構成である。

【0174】上記構成によれば、水溶性染料がベタイン構造を有しているため、上記インクは、酸性条件下でも非常に安定した状態となり保存性が向上する上に、金属塩やゲル化に関わる成分などがほとんど含まれていないため、ノズルでの加熱によるコゲーションの発生を防止できるという効果を奏する。さらに、上記構成では、アルカリ性のインクと組み合わせる使用すれば、カラーブリードを抑制することもできるという効果も奏する。

【0175】上記インクジェット用インクにおいては、上記カチオン界面活性剤が、アミン類の酢酸塩であることが好ましい。

【0176】上記構成によれば、アミン類の酢酸塩を用いることによって、十分なインクの表面張力の調整効果が得られる上に、コゲーションの発生をより一層確実に回避することができるという効果を奏する。

【0177】上記インクジェット用インクにおいては、その pH が 4 以上 7 未満の範囲内に調整されていることが好ましい。

【0178】上記構成によれば、インクの pH が上記弱酸性の状態にあれば、特にアルカリ性のインクと組み合わせることによって、カラーブリードの抑制効果をより一層向上させることができるという効果を奏する。

【0179】また、本発明にかかるインクジェット用インクセットは、上記の課題を解決するために、水性溶媒中に、ベタイン構造を有する水溶性染料およびカチオン

界面活性剤を含んでなるカラーインクと、水性溶媒中に、黒色顔料を含み、かつアルカリ性を示すブラックインクとを含む構成である。

【0180】上記構成によれば、まず、ブラックインクは、アルカリ性条件下で安定して黒色顔料を分散（懸濁）した状態にある一方、カラーインクは、酸性条件下で、ベタイン構造を有する水溶性染料が安定した状態にある。しかも、これら各インクには、金属塩やゲル化に関わる成分などがほとんど含まれていない。そのため、これらインクがノズルで加熱されてもコゲーションの発生が抑制されるという効果を奏する。

【0181】また、ブラックインクとその他のカラーインクとが被記録材上で会合すると、アルカリ性のブラックインクと酸性のカラーインクとが酸-アルカリ反応を起して、これをきっかけとして、黒色顔料は被記録材上で容易かつ迅速に沈殿する。その結果、黒色顔料におけるカラーブリードの発生が抑制されるという効果も奏する。

【0182】さらに、上記ブラックインクおよびカラーインクは、非常に安定した状態にあるので、画像形成の頻度が小さく、画像形成動作の間の時間が長いような場合であっても、黒色顔料や水溶性染料が凝固したり沈殿することがない。そのため優れた保存性を発揮することができるという効果も併せて奏する。

【0183】上記カラーインクの pH は 4 以上 7 未満の範囲内であるとともに、上記ブラックインクの pH は 7 を超えて 10 未満となる範囲内であることが好ましい。

【0184】上記構成によれば、ブラックインクおよびカラーインクの双方の pH が好ましい範囲に調整されることになるので、上記酸-アルカリ反応をより一層効果的に発生させることができるという効果を奏する。

【0185】上記インクジェット用インクセットにおいては、上記ブラックインクに含まれる黒色顔料が、アニオン顔料であることが好ましい。

【0186】上記構成によれば、黒色顔料がアニオン顔料であるため、ブラックインクにおける黒色顔料の分散性がより向上し、ブラックインクの保存性をより一層向上することができるという効果を奏する。また、ブラックインク-カラーインクによる酸-アルカリ反応によるイオン電荷のバランスの崩壊で、アニオン顔料は容易に凝集したり沈殿したりするため、カラー画像形成にお

けるブラックインクのカラーブリードを効果的に抑制することができるという効果も併せて奏する。

【0187】上記インクジェット用インクセットにおいては、上記ブラックインクには、黒色顔料を分散させる分散剤、および画像形成時に被記録材上に黒色顔料を定着させる結着剤の少なくとも一方が含まれていることが好ましい。

【0188】上記構成によれば、分散剤の存在によって、黒色顔料の分散性がさらに向上する。その結果、ブラックインクの保存性を向上させ得るとともに、コゲーションの発生をさらに一層抑制することができるという効果を奏する。また、結着剤の存在によって、黒色顔料の定着がより迅速かつ確実となるので、カラーブリードの発生もさらに一層抑制することができるという効果を奏する。特に、上記分散剤および結着剤の双方を含んでいれば、コゲーションおよびカラーブリードの抑制効果をより向上させることができるとともに、保存性もより向上させることができるという効果を併せて奏する。

【0189】本発明にかかるインクジェット記録方法は、上述したインクジェット用インクセットを用いて、被記録材上に画像を形成する方法である。

【0190】上記方法によれば、アルカリ性条件下で安定なブラックインクと、酸性条件下で安定なカラーインクとが、被記録材上で会合すると、ブラックインクとカラーインクとが酸-アルカリ反応を起して、ブラックインクのイオン電荷のバランスが低下する。そのため、均一に分散している黒色顔料が、非常に容易に沈殿（または凝固）し、黒色顔料は被記録材上で容易かつ迅速に沈殿する。その結果、黒色顔料がカラーブリードを起こさずに定着することになって、カラーブリードを抑制することができるという効果を奏する。

【0191】しかも、従来のように多価金属塩やゲル化のための成分などを含んでいないためコゲーションの発生も抑制することができるとともに、ブラックインクおよびカラーインクが非常に安定した状態にあるので保存性も向上することができるという効果を奏する。

【0192】さらに、多価金属塩とインクとを別々に吐出するような構成を採用する必要がないため、インクヘッドの構成を複雑化を回避して低コスト化することができるとともに、そのメンテナンスも簡素化することができるという効果を奏する。

フロントページの続き

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CLAIMS

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[Claim(s)]

[Claim 1] Ink for ink jets characterized by coming to contain the water soluble dye which has betaine structure, and a cationic surface active agent in an aqueous solvent.

[Claim 2] The above-mentioned cationic surface active agent is ink for ink jets according to claim 1 characterized by being acetate of amines.

[Claim 3] Ink for ink jets according to claim 1 or 2 characterized by adjusting pH within the limits of less than [ 4 or more ] seven.

[Claim 4] The ink set for ink jets characterized by including the color ink which comes to contain the water soluble dye and the cationic surface active agent which have betaine structure in an aqueous solvent, and the black ink which shows alkalinity in an aqueous solvent, including a black pigment.

[Claim 5] pH of the above-mentioned black ink is an ink set for ink jets according to claim 4 with which it is characterized by being within the limits which becomes less than ten exceeding 7 while pH of the above-mentioned color ink is within the limits of less than [ 4 or more ] seven.

[Claim 6] The black pigment contained in the above-mentioned black ink is an ink set for ink jets according to claim 4 or 5 characterized by being an anion pigment.

[Claim 7] Claims 4 and 5 characterized by containing in the above-mentioned black ink either [ at least ] the dispersant which distributes a black pigment, or the binder which fixes a black pigment on a recorded material at the time of image formation, or the ink set for ink jets given in six.

[Claim 8] The ink jet recording approach characterized by forming an image on a recorded material using the ink set for ink jets given in above-mentioned claim 4 thru/or any 1 term of 7.

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the ink for ink jets which makes high-definition image formation possible by controlling not only generating of color bleeding but generating of the so-called Kogation, and raising shelf life further especially, about the ink used for the image formation equipment of an ink jet method.

[0002]

[Description of the Prior Art] The thing of various methods is proposed and put in practical use as image formation equipment for hard copy. Especially, the image formation equipment (ink jet printer) of an ink jet method (drop injection recording method) is preferably used for the application which forms a high-definition color picture in it especially since the cost of the whole equipment can be low held down to the top in which high-definition image formation is possible.

[0003] Here, in the above-mentioned ink jet method, it is known that the trouble called color bleeding or bleeding will occur conventionally.

[0004] That is, by the ink jet method, in order to obtain a color picture, the ink of two or more colors which use water as the main solvent is usually recorded in piles on recorded materials, such as paper. Before the ink of a certain color previously breathed out on the recorded material is established at this time, the ink of other colors will be breathed out one after another, and it will pile up. Therefore, in the part used as the boundary of a different color, the phenomenon, i.e., color bleeding, in which the ink of a different color is spread, or move and the boundary line of each color becomes indefinite, or bleeding (it unifies with color bleeding hereafter) occurs.

[0005] If the above-mentioned color bleeding occurs, since a blot arises between different colors or each color will be in the condition of having been mixed with the ununiformity, image grace is reduced. When color bleeding arises between this black and other colors, the boundary of the image of black bleeds, or it fades, and image grace is made to fall very much especially, although black serves as most important color in image formation.

[0006] Then, the technique which controls generating of this color bleeding is variously proposed from the former. For example, the technique which controls color bleeding is indicated by JP,5-202328,A and JP,6-106375,A by using polyvalent metallic salt for the coagulation of ink.

[0007] By JP,5-202328,A, after supplying a polyvalent-metallic-salt solution on a recorded material previously using the ink containing the color which has at least one carboxyl group, and polyvalent metallic salt, specifically, ink is supplied. While ink dries quickly on a recorded material and generating of color bleeding is controlled by this, the water resisting property of the ink after desiccation can also be raised.

[0008] Moreover, in JP,6-106735,A, each ink of yellow, a Magenta, and cyanogen contains the surface active agent or permeability solvent which gives permeability, and the salt, and the ink of black contains the component which causes thickening or condensation by operation of the above-mentioned salt. By this, while controlling generating of color bleeding, the homogeneity of image concentration can be raised and the grace of black can be raised further.

[0009] Furthermore, in JP,8-209049,A, the technique using the 2nd constituent including the gelation initiation kind which reacts with the 1st constituent including a gel formation kind and this 1st

constituent, and forms gel is indicated. With this technique, generating of color bleeding is controlled by making gel form in the field which adjoins the class product between discharge and each field.

[0010] Moreover, in addition to using the above-mentioned polyvalent metallic salt, in JP,9-207424,A, the technique of making ink containing a pigment and a resin emulsion is indicated. By the interaction with polyvalent metal ion, the above-mentioned resin emulsion controls osmosis of a coloring component, and promotes fixing to a recorded material. Moreover, a resin emulsion can form a coat on a recorded material, and can also raise the scuff resistance of printed matter. If a pigment is furthermore used, it will become possible to control osmosis of the coloring component in ink more. Color bleeding is controlled further further by such operation.

[0011] In addition, in JP,11-349878,A, the interaction of ion is produced between black ink and color ink, and the technique which controls color bleeding is indicated. While making black ink contain an anion pigment, color ink is made to contain the component (for example, a cationic surface active agent and a cation salt) which supplies a cation with this technique. Consequently, the interaction of the ion between black ink-color ink arises, and generating of color bleeding is controlled.

[0012] By the way, it is also known that the trouble which heats ink at the heater in a nozzle in an instant, and is called [ by the pressure of the generated air bubbles ] a Kogation also in the above-mentioned ink jet method in the thermal jet method which makes ink breathe out in addition to the above-mentioned color bleeding from a nozzle will occur.

[0013] Generally the inorganic impurity of the matter produced by the pyrolysis of the coloring component in ink and the minute amount contained in ink, an aggregate, etc. adhere and deposit a Kogation on the above-mentioned heater, and it means the phenomenon [ the regurgitation of the ink by which it becomes impossible for ink heating at a heater to fully have carried out, and it was stabilized as a result ] no longer maintaining. It is known that the inorganic ion in ink (especially metal ion) will have big effect on generating of this Kogation especially.

[0014] For example, when the cation salt is contained in the presentation of ink, by heating on a heater the inorganic ion which forms this cation salt, it reacts with other presentations of ink and insoluble matter may be formed. If such insoluble matter adheres and deposits on a heater, the above-mentioned Kogation will occur.

[0015]

[Problem(s) to be Solved by the Invention] Here, in the Prior art mentioned above, avoiding generating of the above-mentioned Kogation of what can control color bleeding to some extent has invited the trouble of being difficult.

[0016] The ion of this polyvalent metallic salt generates a Kogation, and it stops first, being able to carry out the regurgitation of the ink from a head normally with the technique of using polyvalent metallic salt for the coagulation of ink. Therefore, with each technique of above-mentioned JP,5-202328,A, JP,6-106375,A, and JP,9-207424,A, the reaction mixture and ink containing polyvalent metallic salt are separately breathed out on a recorded material (paper), respectively, and reaction mixture and ink are mixed on this recorded material. However, with the technique which carries out the regurgitation of two kinds of components separately in this way, the structure of an ink head becomes complicated, a manufacturing cost is raised upwards and the trouble of also making control and a maintenance of image formation make it complicated is invited.

[0017] On the other hand, since the combination of the gel formation kind included in the 1st-2nd constituent or a gelation initiation kind becomes the cause of generating a Kogation, in JP,8-209049,A, the trouble that practicality is missing applying to a thermal jet method too is invited.

[0018] Furthermore, in JP,11-349878,A, most matter used as the factor which generates the Kogation of polyvalent metallic salt, the gel formation kind, the gelation initiation kind, etc. which were mentioned above is not included. Therefore, the theory top is possible for generating of color bleeding controlling generating of a Kogation. However, it is indispensable to use a cation salt or a cationic surface active agent with this technique. Although these matter is stable under acid conditions, since the unnecessary matter will be generated in water and effect will be lost if alkali etc. is blended, ink must show acidity.

[0019] When ink shows acidity, the color and pigment which are contained as a color component will be solidified, will become easy to precipitate, consequently will usually produce a big problem at the shelf life and stability of ink. Thus, if the shelf life and stability of ink fall, possibility that coagulation

and precipitate will arise within the head of thermal jet at the time of image formation cannot become high, either, and cannot control generating of a Kogation certainly as a result.

[0020] Furthermore, with the technique of above-mentioned JP,11-349878,A, although it is describing adjusting pH in order to optimize many properties of ink, about the range of concrete pH, reference is not made at all. Therefore, in the above-mentioned technique, concrete measures are not taken at all about the fall of the shelf life by coagulation or precipitate of a color or a pigment.

[0021] Generally, the sulfonic group and the carboxyl group are contained in most colors and pigments. Therefore, if a cationic surface active agent and a cation salt are added to the ink containing these colors or a pigment, an aggregate will produce [ the above-mentioned sulfonic group, a carboxyl group, and a cationic surface active agent or a cation salt ] an acid-alkaline reaction in a lifting and ink easily. Therefore, the ink containing the above-mentioned cationic surface active agent, a cation salt, etc. serves as a presentation which an aggregate tends to generate according to an acid-alkaline reaction.

[0022] It is not only easy to generate an aggregate in ink, but in such ink, condensation significant work increases with the passage of time, or size becomes large. Therefore, in order that an aggregate occurs, and it becomes easy to get it blocked to leave it for a long period of time in the ink passage in an ink cartridge, and it bars the regurgitation of ink upwards, and this aggregate may adhere and accumulate and may cause a Kogation on the above-mentioned heater, heating by which the ink at a heater was stabilized is barred and the regurgitation of ink becomes unstable.

[0023] That is, the ink of the presentation containing a cationic surface active agent or a cation salt not only tends to cause a Kogation, but since an aggregate occurs with time, the shelf life of ink will fall. Consequently, finally, the regurgitation capacity of ink declines irreversibly and invites the trouble that the life of an ink cartridge is also shortened.

[0024] It is in this invention being made in view of the above-mentioned trouble, and the purpose controlling generating of color bleeding or a Kogation certainly, and also raising shelf life, avoiding complication of the configuration of an ink head further, and offering the ink for ink jets which can be used suitable for the image formation equipment of a thermal jet method.

[0025]

[Means for Solving the Problem] As a result of inquiring wholeheartedly in view of the above-mentioned trouble, while this invention persons produce the interaction of ion between color ink and black ink By using what has betaine structure at the end as a color contained in the ink used as color ink It came to complete a header and this invention for it being possible to be able to control not only color bleeding but generating of a Kogation upwards, and to also raise shelf life.

[0026] That is, the ink for ink jets concerning this invention is characterized by coming to contain the water soluble dye which has betaine structure, and a cationic surface active agent in an aquosity solvent, in order to solve the above-mentioned technical problem.

[0027] Usually, according to the above-mentioned configuration, although the trouble which the above-mentioned ink serves as acidity and water soluble dye solidifies occurs under conditions with a cationic surface active agent, since the above-mentioned water soluble dye has betaine structure, also under acid conditions, it will be in the condition of having been stabilized very much, and the shelf life of ink will improve. And a metal salt, the component in connection with gelation, etc. are hardly contained in the above-mentioned ink. Therefore, even if heated with a nozzle, a Kogation is hardly produced. Furthermore, with the above-mentioned configuration, if it is used combining alkaline ink, color bleeding can also be controlled.

[0028] In the above-mentioned ink for ink jets, it is desirable that the above-mentioned cationic surface active agent is acetate of amines.

[0029] According to the above-mentioned configuration, by using the acetate of amines, the adjustment effectiveness of the surface tension of sufficient ink is acquired upwards, and generating of a Kogation can be avoided much more certainly.

[0030] In the above-mentioned ink for ink jets, it is desirable that the pH is adjusted within the limits of less than [ 4 or more ] seven.

[0031] If it is in the condition, i.e., a weak acidic condition, that pH of ink was adjusted to above-mentioned within the limits according to the above-mentioned configuration, the depressor effect of color bleeding can be further raised by combining with alkaline ink especially.

[0032] Moreover, the ink set for ink jets concerning this invention is characterized by including the color ink which comes to contain the water soluble dye and the cationic surface active agent which have betaine structure in an aqueous solvent, and the black ink in which alkalinity is shown in an aqueous solvent, including a black pigment, in order to solve the above-mentioned technical problem.

[0033] While it is in the condition of black ink having been stabilized under alkaline conditions and having distributed the black pigment (suspension), first according to the above-mentioned configuration, color ink is in the condition that the water soluble dye which has betaine structure was stabilized under acid conditions. And a metal salt, the component in connection with gelation, etc. are hardly contained in each [ these ] ink. Therefore, generating of a Kogation is controlled even if these ink is heated with a nozzle.

[0034] Moreover, if black ink and other color ink meet on a recorded material, alkaline black ink and acid color ink will cause an acid-alkaline reaction, and will precipitate easily [ a black pigment ] on a recorded material, and quickly taking advantage of this. Consequently, a black pigment is established, without starting color bleeding.

[0035] Furthermore, since the above-mentioned black ink and color ink are in the condition of having been stabilized very much, even if they are a case so that the frequency of image formation may be small and the time amount between image formation actuation may be long, neither a black pigment nor water soluble dye solidifies, or they do not precipitate. Therefore, the outstanding shelf life can be demonstrated.

[0036] While pH of the above-mentioned color ink is within the limits of less than [ 4 or more ] seven, as for pH of the above-mentioned black ink, it is desirable that it is within the limits which becomes less than ten exceeding 7.

[0037] According to the above-mentioned configuration, since it will be adjusted to the range where pH of the both sides of black ink and color ink is desirable, the above-mentioned acid-alkaline reaction can be generated much more effectively.

[0038] In the above-mentioned ink set for ink jets, it is desirable that the black pigment contained in the above-mentioned black ink is an anion pigment.

[0039] According to the above-mentioned configuration, since a black pigment is an anion pigment, the dispersibility of the black pigment in black ink improves more. Consequently, the shelf life of black ink can be improved further. Moreover, in order to depend for the distributed condition of an anion pigment on the balance of the ionic charge in black ink greatly, when the balance of ionic charge collapses according to the acid-alkaline reaction in black ink-color ink, an anion pigment will be condensed easily or will precipitate. Therefore, the color bleeding of the black ink in color picture formation can be controlled effectively.

[0040] In the above-mentioned ink set for ink jets, it is desirable that either [ at least ] the dispersant which distributes a black pigment, or the binder which fixes a black pigment on a recorded material at the time of image formation is contained in the above-mentioned black ink.

[0041] According to the above-mentioned configuration, the dispersibility of a black pigment improves further by existence of a dispersant. Consequently, while raising the shelf life of black ink, generating of a Kogation can be controlled further further. Moreover, by existence of a binder, since fixing of a black pigment becomes quicker and certain, generating of color bleeding can also be controlled further further. If the both sides of the above-mentioned dispersant and a binder are included especially, while being able to raise the depressor effect of a Kogation and color bleeding more, improvement in shelf-life nearby can be carried out.

[0042] The ink jet record approach concerning this invention is characterized by forming an image on a recorded material using the ink set for ink jets mentioned above.

[0043] According to the above-mentioned approach, if black ink stable under alkaline conditions and color ink stable under acid conditions meet on a recorded material, black ink and color ink will cause an acid-alkaline reaction, and the balance of the ionic charge of black ink will fall. Therefore, the black pigment currently distributed to homogeneity precipitates very easily (or coagulation), and a black pigment precipitates easily and quickly on a recorded material. Consequently, a black pigment will be established without starting color bleeding, and can control color bleeding.

[0044] And since neither polyvalent metallic salt nor the component for gelation is included like before, while also being able to control generating of a Kogation, since it is in the condition that black

ink and color ink were stabilized very much, shelf life will also improve. Furthermore, the maintenance can also be simplified, while being able to avoid complication and being able to low-cost-ize the configuration of an ink head, since it is not necessary to adopt a configuration which carries out the regurgitation of polyvalent metallic salt and the ink separately.

[0045]

[Embodiment of the Invention] It will be as follows if one gestalt of operation of this invention is explained. In addition, this invention is not limited to this.

[0046] Especially the ink for ink jets concerning this invention is suitably used as color ink for color picture formation, and comes to contain the water soluble dye which has betaine structure in an aqueous solvent, and a cationic surface active agent. Therefore, a high-definition image can be formed good, controlling generating of color bleeding and a Kogation and demonstrating high shelf life.

[0047] Moreover, while the ink set concerning this invention is ink in which the presentation in which this black ink contains a black pigment in an aqueous solvent is made indispensable, and alkalinity is shown coming [ at least one kind of color ink, and one kind of black ink ], the above-mentioned color ink is ink in which the presentation which contains the water soluble dye which has betaine structure, and a cationic surface active agent in an aqueous solvent is made indispensable, and acidity is shown.

[0048] That is, the ink jet record approach concerning this invention forms a color picture using color ink and black ink, and serves as a presentation with respectively different color ink and black ink.

[0049] Although water soluble dye is contained in the color ink concerning this invention as an indispensable component, this water soluble dye has betaine structure.

[0050] The betaine structure in this invention points out the structure which the compound which forms dipolar ion according to the structure which the betaine of a wide sense has, i.e., inner salt, and exists as dipolar ion in a solution has. If it puts in another way, it will be defined as the betaine said by this invention as an inner salt mold compound which has cation (cation) structures (it considers as an inner salt machine nature machine), such as for example, a quaternary-ammonium-salt radical, and anion (anion) structures (it considers as an intramolecular acidic group), such as a carboxyl group and a sulfonic group, in one intramolecular.

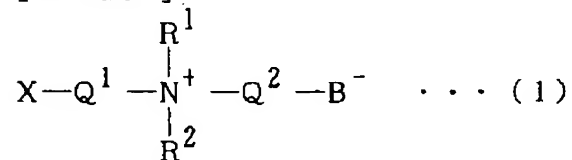
[0051] Therefore, since the water soluble dye in this invention has the above-mentioned betaine structure, it forms dipolar ion with inner salt, even if an aqueous solvent is acidity and it is alkalinity, it is stabilized, and is dissolved in this aqueous solvent. Consequently, generating of the trouble that water soluble dye solidifies or precipitates is avoidable.

[0052] As the above-mentioned water soluble dye, especially if it has the above-mentioned betaine structure, it is not limited, but when basic structure of this water soluble dye is set to X in various water soluble dye, specifically, what has two kinds of structures as follows where the 4th class ammonium structure is included as an inner salt machine nature machine can be mentioned.

[0053] i) — a chain compound — the atomic group which contains the water soluble dye of the basic structure X among four atomic groups combined with the nitrogen atom in the 4th class ammonium structure of a chain type (there may be a side chain) as shown with the following structure expression (1), and intramolecular acidic group B- Structure where every one included atomic group is contained, respectively.

[0054]

[Formula 1]

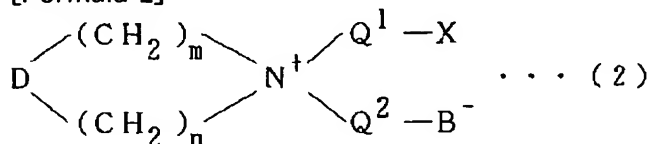


[0055] However, it sets in the above-mentioned structure expression (1), and is R1. And R2 The alkyl group of carbon numbers 1-4 is shown, and it is Q1 independently, respectively. I may not be, or the alkylene structure or oxy-alkylene structure of an oxygen atom and a carbon number 1-2 is shown, and Q2 shows the alkylene structure or oxy-alkylene structure of carbon numbers 1-4.

[0056] ii) a cyclic compound — the atomic group and intramolecular acidic group B<sup>-</sup> which contain the water soluble dye of the basic structure X in the nitrogen atom in the 4th class ammonium structure of a nitrogen-containing monocycle type heterocyclic compound as shown with the following structure expression (2) Structure which the included atomic group has combined one [ at a time ], respectively.

[0057]

[Formula 2]



[0058] However, in the above-mentioned structure expression (2), n and m are the integers of 1 or 2 independently, respectively, and it is Q1. I may not be, or the alkylene structure or oxy-alkylene structure of an oxygen atom and a carbon number 1-2 is shown, and it is Q2. The alkylene structure or oxy-alkylene structure of carbon numbers 1-4 is shown, and D shows an oxygen atom and the alkylene structure of a carbon number 1-2.

[0059] As a suitable example of water soluble dye expressed with the above-mentioned basic structure X As a color of yellow, the acid yellow 23, the direct yellow 86, etc. for example, as a color of a Magenta The reactive red 58, the reactive red 120, the reactive red 180, acid red 52, acid red 214, etc. as a color of cyanogen Although the acid blue 7, the acid blue 9, the direct blue 86, the direct blue 199, etc. are mentioned, it is not limited especially and well-known water soluble dye can be conventionally chosen suitably according to a color to make it color as color ink.

[0060] The above-mentioned intramolecular acidic group B<sup>-</sup> Although it is not limited especially if it is the atomic group which shows acidity, a sulfonic group (-SO<sub>3</sub><sup>-</sup>) and a carboxyl group (-COO<sup>-</sup>) can be mentioned preferably, for example.

[0061] Above R1 Or R2 As an alkyl group of the carbon numbers 1-4 shown, a methyl group (CH<sub>3</sub>-), an ethyl group (C<sub>2</sub>H<sub>5</sub>-), a propyl group (C<sub>3</sub>H<sub>7</sub>-), butyl (C<sub>4</sub>H<sub>9</sub>-), and an isopropyl group (CH<sub>3</sub>) (2 CH-) are mentioned, for example.

[0062] Above Q1 As alkylene structure of the carbon number 1-2 shown, methylene (-CH<sub>2</sub>-) and ethylene (-C<sub>2</sub>H<sub>4</sub>-) are mentioned, and oxy-methylene (-OCH<sub>2</sub>-) and oxyethylene (-OC<sub>2</sub>H<sub>4</sub>-) are mentioned as oxy-alkylene structure. Moreover, the above Q2 As alkylene structure of the carbon numbers 1-4 shown Methylene (-CH<sub>2</sub>-), ethylene (-C<sub>2</sub>H<sub>4</sub>-), trimethylene (-C<sub>3</sub>H<sub>6</sub>-), Tetramethylen (-C<sub>4</sub>H<sub>8</sub>-) is mentioned. As oxy-alkylene structure Oxy-methylene (-OCH<sub>2</sub>-), oxyethylene (-OC<sub>2</sub>H<sub>4</sub>-), oxy-trimethylene (-OC<sub>3</sub>H<sub>6</sub>-), and oxy-tetramethylen (-OC<sub>4</sub>H<sub>8</sub>-) are mentioned.

[0063] As alkylene structure of the carbon number 1-2 shown by Above D, each structure of the above-mentioned methylene and ethylene is mentioned. Since an oxygen atom is sufficient as this D, specifically as a nitrogen-containing monocycle type heterocyclic compound in the above-mentioned structure expression (2), a pyrrolidine, a piperidine, hexamethyleneimine, a morpholine, etc. are mentioned.

[0064] In addition, in this invention, although the most general 4th class ammonium structure as an inner salt machine nature machine was mentioned as the example in the above-mentioned example, if the above-mentioned betaine structure can be formed, it cannot be overemphasized that inner salt machine nature machines may be other base structures.

[0065] As the manufacture approach of the water soluble dye of the betaine structure of having the above (1) or the structure expression of (2), the approach of specifically introducing betaine structure conventionally by the well-known approach, the approach indicated by 86th page - the 88th page of "completely revised version new and a guide to a surfactant" (work: Takehiko Fujimoto and Sanyo Chemical Industries, Ltd.) is mentioned to the water soluble dye expressed with the above-mentioned basic structure X.

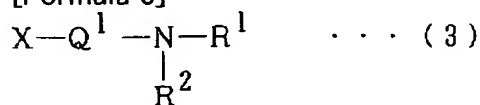
[0066] Specifically, it is the intramolecular acidic group B about the above-mentioned 4th class ammonium structure as an inner salt machine nature machine. - In the case where carry out and a sulfonic group (-SO<sub>3</sub><sup>-</sup>) is chosen, the approach explained below is used suitably.

[0067] First, to the water soluble dye of the above-mentioned basic structure X, tertiary amine

(tertiary amine) structure is conventionally introduced by the well-known approach, and a heterocycle type water-soluble-dye amine as shown in a chain type water-soluble-dye amine as shown in the following structure expression (3), or a structure expression (4) is obtained. In addition, if water soluble dye includes amine structure from origin, it can be used as it is.

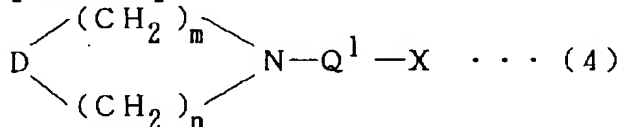
[0068]

[Formula 3]



[0069]

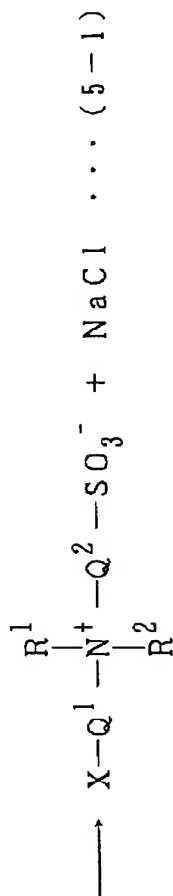
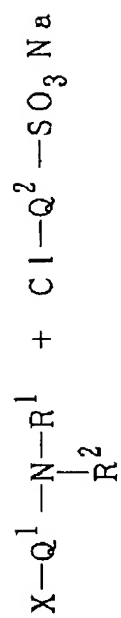
[Formula 4]



[0070] Next, the water-soluble-dye amine of one of the above and chloro alkyl sulfonic-acid sodium of carbon numbers 1-4, Or chloro alkyloxy sulfonic-acid sodium (any compound expresses with  $\text{Cl}-\text{Q}2-\text{SO}_3 \text{Na}$ ) is added and mixed in a suitable solvent, if . while stirring at 60-80 degrees C for several hours — the following reaction formula (5-1) — a reaction is advanced, a sulfonic group is introduced into tertiary amine structure, and or (5-2) obtains the betaine structure.

[0071]

[Formula 5]



[0072]

[Formula 6]





into a cation anion in a water solution, it is not desirable.

[0075] It will not be limited especially if the part which dissociates to ion in an aqueous solvent and serves as a cation (cation) as a cationic surface active agent contained in the color ink concerning this invention as an indispensable component is the matter in which surface activity is shown. Therefore, each cationic surface active agent it is well-known that it can be used for the ink for ink jets is applicable to this invention.

[0076] Specifically, an amine salt, quaternary ammonium salt, sulfonium salt, phosphonium salt, carboxy betaine, aminocarboxylate, lecithin, SAPAMINA (Ciba-Geigy make), AKOBERUG (made in Arnold Hoffmann), etc. can be mentioned. Also in the above, an amine salt and quaternary ammonium salt are desirable, and the acetate (amine acetate) of amines, the acetate of the 4th class ammonium, or a chloride salt is more desirable especially.

[0077] As an example of the acetate of amines, the for example longest hydrophobic group is an alkyl group of carbon numbers 12-18 within the limits, and the acetate of the amines chosen from primary amine, secondary amine, tertiary amine, and the group that consists of those mixture etc. is mentioned preferably. As acetate of such amines, lauryl amine acetate etc. is mentioned, for example.

[0078] If the carbon number of the above-mentioned hydrophobic group becomes 11 or less, hydrophobicity will fall and it will be easy to become a hydrophilic property. On the other hand, if a carbon number becomes 19 or more, hydrophobicity will improve too much. That is, since the balance of the hydrophilic group as a cationic surface active agent and a hydrophobic group collapses and it becomes impossible to demonstrate the good surface activity effectiveness (namely, the adjustment effectiveness of the surface tension mentioned later) when the carbon number of the above-mentioned hydrophobic group separates from within the limits of 12-18, it is not desirable.

[0079] Moreover, as an example of quaternary ammonium salt, poly propoxy quaternary ammonium salt, such as the 4th class ammonium acetate of poly propoxy and the 4th class ammonium chloride of poly propoxy, is used preferably, for example. Each these poly propoxy quaternary ammonium salt is WITCO Corporation. Emcol It is marketed as series etc.

[0080] As an example of the counter ion which can be combined with the above-mentioned cationic surface active agent, acetic-acid ion, formic-acid ion, chloride ion, gluconic-acid ion, succinic-acid ion, tartaric-acid ion, glutaric-acid ion, malonic-acid ion, carboxylic-acid ion, fumaric-acid ion, malic-acid ion, sebacic-acid ion, adipic-acid ion, stearic acid ion, oleic acid ion, lauric-acid ion, benzoic-acid ion, citric-acid ion, etc. are mentioned. Especially, as mentioned above, acetic-acid ion and chloride ion are desirable, and acetic-acid ion is much more desirable.

[0081] The above-mentioned cationic surface active agent is added in order to adjust the surface tension of color ink. It is more desirable to exist in this color ink by the concentration of about 0.5 - 5% of the weight of within the limits, and to have about 3% of the weight of concentration as the concrete content. By containing the cationic surface active agent within the limits of this, it becomes possible to adjust the wettability on the orifice in the head of thermal jet, or a recorded material (paper) good.

[0082] If the content of the above-mentioned cationic surface active agent is less than about 0.5 % of the weight, since the adjustment effectiveness of sufficient surface tension is not acquired, it is not desirable. On the other hand, if it exceeds about 5 % of the weight, since the adjustment effectiveness of surface tension of having balanced the addition will not be acquired upwards, viscosity etc. will become high and the function as color ink will fall, it is not desirable.

[0083] The color ink concerning this invention which comes to contain the water soluble dye which has the above-mentioned betaine structure, and a cationic surface active agent shows acidity, within the limits (it is  $4 \leq \text{pHCl} < 7$  when pH of color ink is set to pHCl) of less than [ 4 or more ] seven has desirable pH, and, specifically, within the limits ( $6 \leq \text{pHCl} < 7$ ) of less than [ 6 or more ] seven has more desirable pH. That is, as for the above-mentioned color ink, it is more desirable that the acescence is shown. Although the color ink applied to this invention by addition of the above-mentioned cationic surface active agent will show the acescence, if acetate and quaternary ammonium salt of amines are especially used as a cationic surface active agent, it can adjust pH within the limits of [ six or more / more desirable ] less than seven.

[0084] In addition, in order to adjust ink to acidity, pH regulator (a buffer/buffer) may be added.

However, in the color ink concerning this invention, what contains a metal salt as a pH regulator cannot be used from the need of avoiding generating of a Kogation.

[0085] As an aqueous solvent contained in the color ink concerning this invention, it comes to contain other still more nearly meltable solvents in water including water at least. Inorganic ion which causes a Kogation is not contained as the above-mentioned water, but although it is not limited especially if it has the purity of extent generally used as an object for ink, ion exchange water (deionized water) is used preferably.

[0086] As a content of the water in color ink, when color ink all weight is made into 100 % of the weight, it is desirable that it is 10 - 90% of the weight of within the limits, and is 30 - 80% of the weight of within the limits, and it is more desirable that it is 50 - 95% of the weight of within the limits.

[0087] It will not be limited especially if the operation of control of generating of the various operations in color ink, i.e., desiccation of ink, coloring or the Kogation in this invention, or color bleeding is not checked as other solvents meltable in the above-mentioned water.

[0088] As a solvent besides the above, specifically For example, a methanol, ethanol, n-propanol, iso-propanol (2-propanol), n-butanol, a sec-butanol, a tert-butanol, an iso-butanol, Alkyl alcohols of the carbon numbers 1-5, such as n-pentanol; Dimethylformamide, Amides, such as dimethylacetamide; Ketones, such as an acetone and diacetone alcohol, or a keto alcohol; tetrahydrofuran, Ether, such as dioxane; Oxypropylene copolymer (polyalkylene glycols); polyethyleneimine; ethylene glycol, such as a polyethylene glycol and a polypropylene glycol, Propylene glycol, a butylene glycol, a trimethylene glycol, Triethylene glycol, 1 and 2, 6-hexane triol, a thioglycol, Hexylene glycol, a diethylene glycol, tetraethylene glycol, Dipropylene glycol, tripropylene glycol, 1,5-pentanediol, Polyhydric alcohol, such as a glycerol; Ethylene glycol monomethyl ether, Ethylene glycol monoethyl ether, the diethylene-glycol monomethyl ether, Diethylene glycol monoethyl ether, the diethylene-glycol monobutyl ether, The low-grade monoalkyl ether of polyhydric alcohol, such as the triethylene glycol monomethyl ether and the triethylene glycol monoethyl ether; Triethylene glycol wood ether, Triethylene glycol diethylether, tetraethylene glycol wood ether, low-grade dialkyl ether [ of polyhydric alcohol, such as tetraethylene glycol diethylether, ]; — trimethylol propane; — monoethanolamine — Organic amines, such as diethanolamine, triethanolamine, 2-pyrrolidone, a N-methyl-2-pyrrolidone, 1,3-dimethyl-2-imidazolidinone, and a sulfolane; various kinds of water-soluble organic solvents urea; etc. are mentioned. The water-soluble above-mentioned organic solvent may be used independently, and may be used also as two or more kinds of mixture.

[0089] Also in the water-soluble above-mentioned organic solvent, the low-grade alkyl ether of polyhydric alcohol, such as polyhydric alcohol, such as alcohol of monovalence, such as iso-propanol (2-propanol), a diethylene glycol, and 1,5-pentanediol, the triethylene glycol monomethyl (or ethyl) ether, and the diethylene-glycol monobutyl ether, trimethylol propane, etc. are desirable especially. Since the alcohol of monovalence is a low-boiling point, the effectiveness of shortening the drying time of color ink at the time of image formation is acquired. Moreover, since the low-grade alkyl ether of polyhydric alcohol or polyhydric alcohol is a high-boiling point, it functions as a wetting agent which controls the desiccation which is not desirable as for color ink.

[0090] Although it is not limited, when color ink all weight is made into 100 % of the weight, especially the content of the water-soluble above-mentioned organic solvent contained in the color ink concerning this invention has 3 - 50% of the weight of desirable within the limits, and 3 - 40% of the weight of its within the limits is more desirable.

[0091] Moreover, when dividing the water-soluble above-mentioned organic solvent into the thing of a low-boiling point, and the thing of a high-boiling point and adding, when color ink is made into 100 % of the weight, in the case of a low-boiling point organic solvent, 0.5 - 10% of the weight of within the limits is desirable, and 1.5 - 6% of the weight of within the limits is more desirable [ in the case of ]. Moreover, when color ink is made into 100 % of the weight, in the case of a high-boiling point organic solvent, 0.5 - 40% of the weight of within the limits is desirable, and it is more desirable. [ of 2 - 20% of the weight of within the limits ]

[0092] In addition, each range where the content of the water-soluble organic solvent mentioned above is desirable shall be included, also when each water-soluble organic solvent is used independently, and also when it uses as two or more kinds of mixture. namely, the above — the

desirable range is desirable range as a total content of a water-soluble organic solvent.

[0093] Moreover, in order to acquire a desired physical-properties value, the color ink concerning this invention can attach a defoaming agent, antiseptics, an antifungal agent, etc. other than the component mentioned above if needed, and can add the water soluble dye of other marketing etc. further. About examples and additions, such as these defoaming agents, antiseptics, and an antifungal agent, it is not limited especially unless it has a bad influence on many properties of color ink, and a well-known technique can be used suitably conventionally.

[0094] In the ink set for ink jets concerning this invention, the black ink in which the presentation which contains a black pigment in an aqueous solvent is made indispensable in addition to the color ink containing each above-mentioned component, and alkalinity is shown is included.

[0095] Although the carbon black generally used for black ink can be mentioned as a black pigment contained in the above-mentioned black ink and it is not limited especially, especially the anion pigment charged in anionic is desirable in a water solution by embellishing a carboxyl group on the surface of a black pigment especially.

[0096] The method of obtaining the carbon black which introduced  $\text{-COONa}$  (sodium salt of a carboxyl group) on the surface of carbon black, and was charged in anionic as a concrete example of this anion pigment is mentioned. After often mixing in water and making it distribute acid commercial carbon black, a sodium hypochlorite is specifically dropped and heated to this, the obtained slurry is filtered and rinsed after that and a pigment wet cake is obtained, further, water is made to re-distribute this and it desalts by the reverse osmotic membrane, and although the method of condensing these pigment dispersion liquid is mentioned further, it is not limited especially.

[0097] Furthermore, it is also possible to use commercial self-distributed carbon black as an anion pigment. For example, the self-distributed carbon black "KYABO jet" (a trade name, Cabot make) which the carboxyl group ( $\text{-COO-}$ ) coupled directly and was charged in anionic is mentioned.

[0098] It is very desirable that the dispersant for distributing a black pigment is contained in the above-mentioned black ink. When using especially carbon black which is not self-distributed process input output equipment, it is very desirable that a dispersant is added from the point which avoids precipitate of this carbon black and raises shelf life.

[0099] Specifically as this dispersant, the various resin which has a carboxyl group can be mentioned. If the various resin which has such a carboxyl group is added as a dispersant, as for black ink, alkalinity will be shown and a black pigment, especially an anion pigment will serve as a stable solution (dispersion liquid/suspension) under these conditions. Consequently, even if it leaves it for a long period of time, a pigment precipitating or solidifying is controlled and it can acquire the outstanding shelf life.

[0100] As various resin which has the above-mentioned carboxyl group, a styrene-acrylic-acid copolymer, a styrene-acrylic-acid-acrylic-acid alkyl ester copolymer, a styrene-maleic-acid copolymer, a styrene-maleic-acid-acrylic-acid alkyl ester copolymer, a styrene-methacrylic-acid copolymer, a styrene-methacrylic-acid-acrylic-acid alkyl ester copolymer, a styrene-maleic-acid half ester copolymer, a vinyl naphthalene-acrylic-acid copolymer, vinyl naphthalene-maleic-acid copolymers, or these salts are mentioned, for example. Especially, styrene-acrylic resin is desirable and especially a styrene-acrylic-acid copolymer is desirable.

[0101] When the whole black ink is made into 100 % of the weight, as for various kinds of above-mentioned resin, it is desirable to contain by 0.1 - 5% of the weight of within the limits, and it is more desirable to contain by 0.3 - 2% of the weight of within the limits.

[0102] In addition, a thing usable also as a binder mentioned later is also contained in various kinds of above-mentioned resin. In that case, since the number of components added by black ink decreases, preparation of black ink can be simplified.

[0103] Moreover, as the above-mentioned dispersant, a resin emulsion is mentioned to others. A continuous phase is water and the resin emulsion said here means the emulsion whose dispersed phases are the following resinous principles.

[0104] As a resinous principle of the dispersed phase in the above-mentioned resin emulsion, acrylic resin, vinyl acetate system resin, styrene-butadiene resins, vinyl chloride system resin, acrylic-styrene resin, butadiene system resin, styrene resin, bridge formation acrylic resin, bridge formation styrene resin, benzoguanamine resin, phenol resin, silicone resin, an epoxy resin, etc. are mentioned.

[0105] The above-mentioned resin emulsion can be obtained by carrying out the distributed polymerization (emulsion polymerization) of the resin monomer underwater with a surfactant according to a situation. For example, the emulsion of acrylic resin or styrene-acrylic resin is obtained by carrying out the distributed polymerization of acrylic ester (meta) or (meta) acrylic ester, and the styrene underwater with a surfactant.

[0106] the rate of the resin as the above-mentioned dispersed phase component, and water — the resin 100 weight section — receiving — water 60 — the 400 weight sections — within the limits of the 100 — 200 weight section is preferably suitable.

[0107] Moreover, it is also possible to use a commercial resin emulsion. as a commercial resin emulsion — the micro gel E-1002 and E-5002 (a styrene-acrylic resin emulsion —) the Nippon Paint Co., Ltd. make and BONKOTO 4001 (an acrylic resin emulsion —) the Dainippon Ink & Chemicals, Inc. make and BONKOTO 5454 (a styrene-acrylic resin emulsion —) The Dainippon Ink & Chemicals, Inc. make, SAE-1014 (a styrene-acrylic resin emulsion, Nippon Zeon Co., Ltd. make), SAIBI Norian SK-200 (an acrylic resin emulsion, SAIDEN CHEMICAL INDUSTRY CO., LTD. make), etc. are mentioned.

[0108] When the above-mentioned resin emulsion makes black ink 100 % of the weight at this invention, it is desirable to be contained at 0.1 — 40% of the weight of within the limits, and it is more desirable to be contained at 1 — 25% of the weight of within the limits.

[0109] Moreover, as a dispersant in this invention, both the resin which has the above-mentioned carboxyl group, and the above-mentioned resin emulsion may be contained. Furthermore, when a black pigment is an anion pigment with high dispersibility, the dispersant does not necessarily need to be contained.

[0110] Furthermore, the binder which fixes a black pigment on a recorded material at the time of image formation may be contained in the above-mentioned black ink. As this binder, for example Polyurethane resin, starch, gelatin, Water soluble polymers, such as a latex, casein, gum arabic, sodium alginate, and polyacrylamide; Methyl cellulose, Cellulosics, such as a carboxy cellulose and a hydroxymethyl cellulose; Polyacrylate, A vinyl naphthalene-acrylic-acid copolymer, a styrene-maleic-acid copolymer, and its salt, Anionic (anion nature) giant molecules, such as sodium salt of beta-naphthalene sulfonic-acid formalin condensation product, and phosphate; the Nonion nature (nonionic) giant molecules, such as polyvinyl alcohol, a polyvinyl pyrrolidone, and a polyethylene glycol, etc. are mentioned.

[0111] When black ink is made into 100 % of the weight, as for the content of the above-mentioned binder, it is desirable to contain by 0.5 — 30% of the weight of within the limits. If it is less than 0.5 % of the weight, the effectiveness by adding a binder will not be acquired. On the other hand, if it exceeds 30 % of the weight, since the effectiveness corresponding to an addition will not be acquired upwards, viscosity etc. will become high and the function as black ink will fall, it is not desirable.

[0112] It comes to contain other still more nearly meltable solvents in water including water at least like the color ink mentioned above as an aqueous solvent contained in the above-mentioned black ink. Since it is the same as that of the water-soluble organic solvent illustrated by explanation of the color ink which each mentioned above also as other solvents also as the above-mentioned water, the detailed explanation is omitted.

[0113] The above-mentioned black ink has desirable within the limits (it is  $7 < \text{pHBk} \leq 10$  when pH of black ink is set to pHBk) from which it indicates that alkalinity mentioned above, and pH exceeds 7 and specifically becomes ten or less, and its within the limits ( $7 < \text{pHBk} \leq 9$ ) which pH exceeds 7 and becomes nine or less is more desirable. That is, as for the above-mentioned black ink, it is more desirable that alkalescence is shown.

[0114] It is very desirable that organic amines, such as 2-pyrrolidone, are contained in the above-mentioned black ink also in the water-soluble organic solvent mentioned above here, for example. While these organic amines function as a pH regulator (a buffer/buffer) which adjusts black ink to alkalescence, a Kogation is preferably used, in order not to cause. Moreover, when black ink is made into 100 % of the weight, as for the content, it is desirable to contain by 0.001 — 10% of the weight of within the limits.

[0115] Moreover, in order to acquire a desired physical-properties value, the black ink concerning this invention can attach a defoaming agent, antiseptics, an antifungal agent, etc. other than the component mentioned above if needed, and can add the water soluble dye of other marketing etc.

further. About examples and additions, such as these defoaming agents, antiseptics, and an antifungal agent, it is not limited especially unless it has a bad influence on many properties of black ink, and a well-known technique can be used suitably conventionally.

[0116] The ink set containing the color ink, and this color ink and the above-mentioned black ink as ink for ink jets concerning this invention concerning this invention is widely applicable to various well-known ink jet printers conventionally.

[0117] As a typical method of the above-mentioned ink jet printer, the piezo jet method which carries out the regurgitation of the ink in a nozzle according to physical deformation of a piezo-electric element, and the thermal jet method which carries out the regurgitation with the air bubbles which apply heat to the ink in a nozzle and are generated are held. the ink set concerning this invention — the above — although it can use suitable for any method, it is especially used for the thermal jet method which a Kogation tends to generate by heating ink especially preferably.

[0118] In the above-mentioned ink jet recording method, the above-mentioned black ink and color ink are separately breathed out from the nozzle of a head, respectively, and contact mutually by forming an image in the paper as a recorded material.

[0119] Here, especially at the former, the phenomenon, i.e., color bleeding, in which each ink is spread, or move and the boundary line of each color becomes indefinite occurs in the part used as black and a boundary with other colors. Consequently, the boundary of the image of black bleeds, or it fades, and image grace is made to have been to fall very much especially.

[0120] Moreover, the ink component adhered to the heater part of a nozzle from the problem on the presentation of ink, produced the Kogation, or when the frequency of image formation was small and the time amount between image formation actuation was long, the color and pigment of ink solidified, or it precipitated, the nozzle was got blocked, and the trouble that shelf-life also fell was invited.

[0121] On the other hand, in this invention, first, within a head, while it is in the condition of black ink having been stabilized under alkaline conditions and having distributed the black pigment (suspension), color ink is in the condition that the water soluble dye which has betaine structure was stabilized under acid conditions. And a metal salt, the component in connection with gelation, etc. are hardly contained in each [ these ] ink. Therefore, even if it is a case so that a Kogation may not be produced even if heated with a nozzle, and the frequency of image formation may be small and the time amount between image formation actuation may be long, neither a black pigment nor water soluble dye solidifies, or it does not precipitate.

[0122] Furthermore, if black ink and other color ink meet on a recorded material, alkaline black ink and acid color ink will cause an acid-alkaline reaction, and the balance of the ionic charge of black ink will fall. In black ink, in the condition with the good charge balance of ion, although the black pigment is distributing to homogeneity, if the balance falls, since it will become easy to precipitate very easily (or coagulation), a black pigment precipitates easily on a recorded material, and quickly. Consequently, a black pigment will be established without starting color bleeding, and can control color bleeding.

[0123] The inhibition mechanism of the above-mentioned color bleeding is explained more concretely. For example, suppose that color ink contains the water soluble dye of betaine structure, and a cationic surface active agent noting that black ink contains an anion pigment as a black pigment and contains styrene-acrylic resin as a dispersant.

[0124] If these are separately breathed out from a nozzle and meet on a recorded agent, the styrene-acrylic resin which is the dispersant which was distributing the anion pigment good, and the cationic surface active agent of color ink will cause an acid-alkaline reaction. Namely, the carboxyl group in the end of styrene-acrylic resin and the cation which shows the surface activity effectiveness in a cationic surface active agent react, and the ionic charge balance in black ink becomes unstable by making this reaction into a driving force. By this, while an anion pigment precipitates easily, it also solidifies easily the above-mentioned styrene-acrylic resin which was being distributed in black ink.

[0125] Consequently, it solidifies and condenses certainly, without styrene-acrylic resin's making the precipitating anion pigment established, and black ink's not carrying out osmosis to a recorded material, either, but generating color bleeding between color ink.

[0126] Thus, by the ink jet recording method concerning this invention, the fixing reaction of the

black which makes an acid-alkaline reaction a driving force on a recorded material is produced by using alkaline black ink and acid color ink. Consequently, color bleeding is controlled certainly. [0127] And even if it is the ink jet printer of a thermal jet method, it is not made to produce a Kogation especially, since a component which is concerned with a metal salt or a gelation reaction is not contained in each above-mentioned ink. Furthermore, in order to make color bleeding control, if each above-mentioned ink is original, it shows the acidity or alkalinity which is in a condition unstable as ink. However, since the pigment is distributed good with anion-izing and a dispersant while betaine-izing water soluble dye, even if it leaves it for a long period of time, an ink component can solidify, or cannot precipitate, but the trouble that the image formation of the nozzle cannot be got blocked and carried out can also be avoided. Consequently, it is that whose shelf life of ink also improved very much.

[0128]

[Example] Hereafter, although this invention is further explained to a detail based on an example and the example of a comparison, this invention is not limited to these. In addition, in the following explanation, the weight section is only written as the "section" and weight % is also only written as "%."

[0129] Moreover, the following approach estimated color bleeding, a Kogation, and shelf life.

[0130] [Color bleeding] It checked visually whether the blot between different colors at the time of forming an image in a PPC form etc. would occur using the color ink jet printer of a commercial thermal head method, and the boundary of each color would be indefinite. At this time, a blot etc. did not occur at all, but O, a blot, etc. generated the case where the boundary of each color was clear, and the case where the boundary of each color was indefinite was evaluated as x.

[0131] [Kogation] Like evaluation of color bleeding, using the color ink jet printer of a thermal jet method, it was filled up with each color ink to the amount of conventions of an ink cartridge, and the actuation which exhausts each color ink of all by image formation was repeated twice. It checked visually whether at this image formation time, the blur etc. would have occurred in the image. Then, the cartridge was decomposed and the heater part of a thermal head was checked visually.

[0132] At this time, the case where abnormalities, such as a blur, were checked during O and image formation in the case where an unusual condition is not seen at all almost similarly [ before abnormalities, such as a blur, are not checked during image formation and a heater part carries out image formation ], or a certain affix etc. was seen was evaluated as x.

[0133] [Shelf life] Like color bleeding and evaluation of a Kogation, using the color ink jet printer of a thermal jet method, it was filled up with each color ink to the amount of conventions of an ink cartridge, and was kept in the condition as it is for three months by ordinary temperature. Then, the same usual image formation as storage before was carried out using this ink cartridge. And it evaluated about the following three points.

[0134] 1. It is before and after storage of color ink, and the image formation actuation above-mentioned image formation actuation was compared. At this time, the regurgitation of a head to the color ink could not be carried out, but the case where it was not different from before \*\* and storage at all, and the case of good image formation where a blur is seen was completed in the image formed in the case where image formation cannot be carried out after [ although image formation was completed once, ] carrying out image formation to some extent, x and was evaluated as O.

[0135] 2. After ending the image formation actuation after heater storage of a thermal head, the cartridge was decomposed as well as evaluation of a Kogation, and the heater part of a thermal head was checked visually. Almost similarly [ before a heater part carries out image formation ] at this time, the case where O, a certain affix, etc. were seen in the case where an unusual condition is not seen was evaluated as x in any way.

[0136] 3. After ending the image formation actuation after condition storage of ink, the condition of color ink itself was checked visually. At this time, the case where O and a certain aggregate had generated the case where it is not different from before storage and neither coagulation nor precipitate has arisen was evaluated as x.

[0137] The shelf life of color ink was evaluated by synthesizing three above-mentioned evaluations. That is, the case where there was at least one x among the \*\* and above-mentioned three evaluations of the case where there is one or \*\* among the O and above-mentioned three



evaluations of the case where all three above-mentioned evaluations are O was evaluated as x.  
 [0138] [Example 1] In this example, the black ink of the presentation shown in Table 1 and cyanogen, a Magenta, and each color ink of yellow were prepared as an ink set concerning this invention, and image formation was performed using these ink set.

[0139] That is, while using the styrene-acrylic-acid copolymer as a dispersant and using the polyurethane emulsion for carbon black MA 7 (Mitsubishi Chemical make) as a binder as a black pigment, it blended so that it might become pure water (ion exchange water) and the content which shows these in Table 1, using 2-pyrrolidone, the diethylene-glycol monobutyl ether, trimethylol propane, and 2-propanol as other water-soluble organic solvents as a solvent, and the black ink (1) concerning this invention was prepared. pH of this black ink (1) is about 8, and showed alkalescence.

[0140] Next, it is if it will be in charge of preparation of the color ink of cyanogen first if preparation of color ink is explained, Using the direct blue 199 (DAIWA formation make) and the acid blue 9 (DAIWA formation make) as water soluble dye, betaine structure was conventionally introduced by the well-known approach (refer to the gestalt of said operation) to each [ these ] color, and the direct blue 199 betaine-ized derivative and acid blue 9 betaine-ized derivative as water soluble dye which has the betaine structure where it is used for this invention were obtained.

[0141] If similarly in charge of preparation of the color ink of a Magenta, using acid red 52 (DAIWA formation make) and the reactive red 180 (Clariant make) as water soluble dye, betaine structure was conventionally introduced by the well-known approach to each [ these ] color, and the acid red 52 betaine-ized derivative and reactive let 180 betaine-ized derivative as water soluble dye which has the betaine structure where it is used for this invention were obtained.

[0142] If similarly in charge of preparation of the color ink of yellow, using the acid yellow 23 (DAIWA formation make) as water soluble dye, betaine structure was conventionally introduced by the well-known approach, and the acid yellow 23 betaine-ized derivative as water soluble dye which has the betaine structure where it is used for this invention was obtained.

[0143] In addition to each above-mentioned betaine-ized derivative, using lauryl amine acetate as a cationic surface active agent, further, as a solvent, it blended with pure water (ion exchange water) so that it might become the content which shows these in Table 2, using 2-pyrrolidone, trimethylol propane and 1,5-pentanediol, or a diethylene glycol as other water-soluble organic solvents, and cyanogen, a Magenta, and each color ink (1) of yellow were prepared. pH of each [ these ] color ink (1) is about 5-6, and all showed the acescence.

[0144]

[Table 1]

		成 分 名	含有量 (重量%)
黒色顔料		カーボンブラックMA7	5
分散剤		スチレン-アクリル酸共重合体	1
結着剤		ポリウレタンエマルジョン	2
水性 溶媒	水溶性有機溶剤	2-ピロリドン	6
		ジエチレングリコールモノブチルエーテル	6
		トリメチロールプロパン	6
		2-プロパノール	2
	水	純 水	(残 量)
計		ブラックインク(1)	100

[0145]



[Table 2]

	シアインク (1)		マゼンタインク (1)		イエローインク (1)	
	成分名	含有量 (重量%)	成分名	含有量 (重量%)	成分名	含有量 (重量%)
水溶性染料の ペダイン化 誘導体	ダイレクトブルー 199 誘導体	2	アシッドレッド52 誘導体	0.5	アシッドイエロー 23 誘導体	2.5
	アシッドブルー9 誘導体	1	リアクティブレッド 180 誘導体	2.5		
カチオン 界面活性剤	ラウリルアミン酢酸 塩	2	ラウリルアミン酢酸 塩	2	ラウリルアミン酢酸 塩	3
水性 有機溶媒	トリメチロールプロ パン	6	トリメチロールプロ パン	6	トリメチロールプロ パン	7
	2-ピロリドン	6	2-ピロリドン	6	2-ピロリドン	4
	1,5-ベンタンジオ ール	7	1,5-ベンタンジオ ール	7	ジエチレングリコ ール	4
水	純水	(残 量)	純水	(残 量)	純水	(残 量)
計		100		100		100

[0146] In addition, in above-mentioned after-mentioned Table 2, 4, and 5, the betaine-ized derivative of water soluble dye is only written as "the derivative (name of water soluble dye)." Moreover, although there is no publication a "derivative" in the water soluble dye indicated to the after-mentioned Table 6 and 7, this shows that it is water soluble dye with the origin which does not introduce betaine structure, and differs from the above-mentioned betaine-ized derivative.

[0147] The ink cartridge of head one apparatus in the color ink jet printer of the thermal head method mentioned above was filled up with the above-mentioned black ink (1). Moreover, it was filled up with the above-mentioned cyanogen, a Magenta, and each color ink (1) of yellow until it became the amount of conventions at the ink cartridge of 3 color one apparatus and head one apparatus in the above-mentioned color ink jet printer.

[0148] As a recorded material, using the PPC form generally used, image formation was performed using the above-mentioned ink cartridge until it consumed each above-mentioned color ink (1)

completely. Furthermore, after that, it was filled up with each above-mentioned color ink (1) until it became the amount of conventions at the ink cartridge, and image formation was performed until it consumed each color ink (1) completely again.

[0149] Then, the image formed on the form was checked visually and it evaluated about color bleeding. Moreover, after image formation termination, the ink cartridge was decomposed, the heater part of an ink head was observed visually, and it evaluated about the Kogation. An evaluation result is shown in the after-mentioned table 8.

[0150] Furthermore, after keeping each above-mentioned color ink (1) for three months in the condition [ having filled up the ink cartridge ], image formation was performed like the above. The image with which it was formed [ with which were formed and it image-formation-operated ] after this storage was evaluated about shelf life by comparing storage before. An evaluation result is shown in the after-mentioned table 8.

[0151] [Example 2] In this example, the black ink of the presentation shown in Table 3 and cyanogen, a Magenta, and each color ink of yellow were prepared as an ink set concerning this invention, and image formation was performed using these ink set.

[0152] While using the polyurethane emulsion as a binder, using commercial self-distributed carbon black "KYABO jet" (a trade name, Cabot make) as a black pigment, it blended so that it might become pure water (ion exchange water) and the content which shows these in Table 3, using 2-pyrrolidone, the diethylene-glycol monobutyl ether, polyethyleneimine, and 2-propanol as other water-soluble organic solvents as a solvent, and the black ink (2) concerning this invention was prepared. pH of this black ink (2) is about 8, and showed alkalescence.

[0153] Next, if first in charge of preparation of the color ink of cyanogen when preparation of color ink was explained, using the acid blue 7 (DAIWA formation make) as water soluble dye, betaine structure was conventionally introduced by the well-known approach, and the acid blue 7 betaine-ized derivative as water soluble dye which has the betaine structure where it is used for this invention was obtained.

[0154] If similarly in charge of preparation of the color ink of a Magenta, using acid red 52 (DAIWA formation make) and the reactive red 58 (DAIWA formation make) as water soluble dye, betaine structure was conventionally introduced by the well-known approach to each [ these ] color, respectively, and the acid red 52 betaine-ized derivative and reactive let 58 betaine-ized derivative as water soluble dye which has the betaine structure where it is used for this invention were obtained.

[0155] If similarly in charge of preparation of the color ink of yellow, using the acid yellow 23 (DAIWA formation make) as water soluble dye, betaine structure was conventionally introduced by the well-known approach, and the acid yellow 23 betaine-ized derivative as water soluble dye which has the betaine structure where it is used for this invention was obtained.

[0156] In addition to each above-mentioned betaine-ized derivative, using lauryl amine acetate as a cationic surface active agent, further, as a solvent, it blended with pure water (ion exchange water) so that it might become the content which shows these in Table 4, using polyethyleneimine, 2-pyrrolidone and 1,5-pentanediol, or a diethylene glycol as other water-soluble organic solvents, and cyanogen, a Magenta, and each color ink (2) of yellow were prepared. pH of each [ these ] color ink (2) is about 5-6, and all showed the acescence.

[0157]

[Table 3]

		成 分 名	含有量 (重量%)
黒色顔料		キャボジェット	5
分散剤		—	—
結着剤		ポリウレタンエマルジョン	2
水性 溶 媒	水溶性有機溶剤	2-ピロリドン	6
		ジエチレングリコールモノブチルエーテル	6
		ポリエチレンイミン	6
		2-プロパノール	2
	水	純 水	(残 量)
計		ブラックインク (2)	100

[0158]

[Table 4]

	シアインク (2)		マゼンタインク (2)		イエローインク (2)	
	成分名	含有量 (重量%)	成分名	含有量 (重量%)	成分名	含有量 (重量%)
水性染料の ペタイン化 誘導体	アシッドブルー-7 誘導体	3	アシッドレッド52 誘導体	0.5	アシッドイエロー 23誘導体	2.5
			リアクティブレッド 58誘導体	2.5		
カチオン 界面活性剤	ラウリルアミン酢酸 塩	2	ラウリルアミン酢酸 塩	2	ラウリルアミン酢酸 塩	3
水性 有機溶剤	ポリエチレニンミン	6	ポリエチレニンミン	6	ポリエチレニンミン	7
	2-ピロリドン	6	2-ピロリドン	6	2-ピロリドン	4
水	1,5-ペンタンジオ ール	7	1,5-ペンタンジオ ール	7	ジエチレングリコー ル	4
	純水	(残 量)	純水	(残 量)	純水	(残 量)
計		100		100		100

[0159] The ink cartridge in the color ink jet printer of the thermal head method mentioned above was filled up with the above-mentioned black ink (2) and the above-mentioned cyanogen, a Magenta, and each color ink (2) of yellow like the example 1. And the same image formation as an example 1 was performed, and it evaluated about color bleeding, a Kogation, and shelf life. An evaluation result is shown in the after-mentioned table 8.

[0160] [Example 1 of a comparison] Black ink (1) was prepared like said example 1 (refer to Table 1). Moreover, cyanogen, a Magenta, and each comparison color ink (1) of yellow were prepared like said example 1 except having used sodium lauryl sulfate as an anionic surface active agent, without using for the color ink concerning this invention the cationic surface active agent which is an indispensable component. pH of each [ these ] comparison color ink (1) is about 8-9, and all showed alkalinescence. The content of each component in each comparison color ink (1) is shown in Table 5.

[0161]

[Table 5]

	比較シアインク (1)		比較マゼンタインク (1)		比較イエローインク (1)	
	成分名	含有量 (重量%)	成分名	含有量 (重量%)	成分名	含有量 (重量%)
水溶性染料の ベタイン化 誘導体	ダイレクトブルー 1199誘導体	2	アシッドレッド52 誘導体	0.5	アシッドイエロー 23誘導体	2.5
	アシッドブルー9 誘導体	1	リアクティブレッド 180誘導体	2.5		
アニオン 界面活性剤	ラウリル硫酸ナトリ ウム	2	ラウリル硫酸ナトリ ウム	2	ラウリル硫酸ナトリ ウム	3
水性 有機溶剤	トリメチロールプロ パン	6	トリメチロールプロ パン	6	トリメチロールプロ パン	7
	2-ピロリドン	6	2-ピロリドン	6	2-ピロリドン	4
	1,5-ペンタンジオ ール	7	1,5-ペンタンジオ ール	7	ジエチレングリコー ル	4
水	純水	(残 量)	純水	(残 量)	純水	(残 量)
計		100		100		100

[0162] Using the above-mentioned black ink (1) and comparison color ink (1), image formation was performed like said example 1, and it evaluated about color bleeding, a Kogation, and shelf life.

Moreover, an evaluation result is shown in the after-mentioned table 8.

[0163] [Example 2 of a comparison] Black ink (1) was prepared like said example 1 (refer to Table 1).

Moreover, cyanogen, a Magenta, and each comparison color ink (2) of yellow were prepared like said example 1 except not using for the color ink concerning this invention the water soluble dye which has the betaine structure which is an indispensable component. pH of each [ these ] comparison color ink (2) is about 5-6, and all showed the acescence. The content of each component in each comparison color ink (2) is shown in Table 6. In addition, each water soluble dye shown in after-mentioned Table 6 and 7 is the same as each water soluble dye before introducing the betaine structure in said example 1 as it was mentioned above.

[0164]

[Table 6]

	比較シアインク (2)		比較マゼンタインク (2)		比較イエローインク (2)	
	成分名	含有量 (重量%)	成分名	含有量 (重量%)	成分名	含有量 (重量%)
水溶性染料	ダイレクトブルー 199	2	アシッドレッド52	0.5	アシッドイエロー 23	2.5
	アシッドブルー9	1	リアクティブレッド 180	2.5		
カチオン 界面活性剤	ラウリルアミン酢酸 塩	2	ラウリルアミン酢酸 塩	2	ラウリルアミン酢酸 塩	3
水性 有機溶剤	トリメチロールプロ パン	6	トリメチロールプロ パン	6	トリメチロールプロ パン	7
	2-ピロリドン	6	2-ピロリドン	6	2-ピロリドン	4
	1,5-ペンタンジオ ール	7	1,5-ペンタンジオ ール	7	ジエチレングリコー ル	4
水	純水	(残 量)	純水	(残 量)	純水	(残 量)
計		100		100		100

[0165] Using the above-mentioned black ink (1) and comparison color ink (2), image formation was performed like said example 1, and it evaluated about color bleeding, a Kogation, and shelf life.

Moreover, an evaluation result is shown in the after-mentioned table 8.

[0166] [Example 3 of a comparison] Black ink (1) was prepared like said example 1 (refer to Table 1). Moreover, in order to draw a Kogation, in the color ink of this invention, cyanogen, a Magenta, and each comparison color ink (3) of yellow were prepared like said example 1 except having used the magnesium nitrate or calcium nitrate as polyvalent metallic salt (cation salt) which is the component which is not added. pH of each [ these. ] comparison color ink (3) is about 6-7, and all showed the acescence. The content of each component in each comparison color ink (3) is shown in Table 7.

[0167]

[Table 7]

	比較シアソインク (3)		比較マゼンタインク (3)		比較イエローインク (3)	
	成分名	含有量 (重量%)	成分名	含有量 (重量%)	成分名	含有量 (重量%)
水溶性染料	ダイレクトブルー 199	2	アシッドレッド52	0.5	アシッドイエロー 23	2.5
	アシッドブルー9	1	リアクティブレッド 180	2.5		
ノニオン 界面活性剤	アセチレングリコー ル	2	アセチレングリコー ル	2	アセチレングリコー ル	3
多価金属塩	硝酸マグネシウム	3	硝酸マグネシウム	3	硝酸カルシウム	5
水性 有機溶媒	トリメチロールプロ パン	6	トリメチロールプロ パン	6	トリメチロールプロ パン	7
	2-ピロリドン	6	2-ピロリドン	6	2-ピロリドン	4
	1,5-ベンタンジオ ール	7	1,5-ベンタンジオ ール	7	ジエチレングリコー ル	4
水	純水	(残 量)	純水	(残 量)	純水	(残 量)
計		100		100		100

[0168] Using the above-mentioned black ink (1) and comparison color ink (3), image formation was performed like said example 1, and it evaluated about color bleeding, a Kogation, and shelf life. Moreover, an evaluation result is shown in the following table 8.

[0169]

[Table 8]

		実施例 1	実施例 2	比較例 1	比較例 2	比較例 3
ブラック インク	種類	(1)	(2)	(1)	(1)	(1)
	pH	8	8	8	8	8
カラー インク	種類	(1)	(2)	比較(1)	比較(2)	比較(3)
	pH	5~6	5~6	8~9	5~6	6~7
	水溶性染料 のベタイン 化の有無	あ り	あ り	あ り	な し	な し
	界面活性剤	カチオン	カチオン	アニオン	カチオン	ノニオン
	多価金属塩	な し	な し	な し	な し	あ り
カラブリード		○	○	×	○	○
コゲーション		○	○	○	×	×
保管 後	1. 動作	○	○	○	×	△
	2. ヒータ	○	○	○	×	×
	3. インク	○	○	○	×	○
保存性		○	○	○	×	×

[0170] It was possible to have attained prevention of color bleeding, prevention of a Kogation, and all the improvement in shelf life in the case where the ink set for ink jets concerning this invention is used so that clearly from the result of Table 8 (example 1-2). However, if betaine structure was not introduced into water soluble dye, shelf life falls upwards and generating of a Kogation was not able to be prevented, either (example 2-3 of a comparison). When the cation salt was used especially, shelf life got worse very much (example 2 of a comparison).

[0171] On the other hand, when introducing betaine structure into water soluble dye, prevention of a Kogation and improvement in shelf life could fully be attained, but (an example 1-2, example 1 of a comparison) if a cationic surface active agent was not used, generating of color bleeding could not be prevented but image quality deteriorated sharply (example 1 of a comparison).

[0172] Thus, in the ink for ink jets concerning this invention, since it has come to contain the water soluble dye which has betaine structure, and a cationic surface active agent in an aqueous solvent, it can consider as the outstanding ink which can attain prevention of color bleeding, prevention of a Kogation, and all the improvement in shelf life.

[0173]

[Effect of the Invention] As mentioned above, the ink for ink jets concerning this invention is a configuration which comes to contain the water soluble dye which has betaine structure, and a cationic surface active agent in an aqueous solvent.

[0174] Since water soluble dye has betaine structure according to the above-mentioned configuration, since it will be in the condition of having been stabilized very much, shelf life improves upwards also under acid conditions and a metal salt, the component in connection with gelation, etc. are hardly contained, the above-mentioned ink does so the effectiveness that generating of the Kogation by heating with a nozzle can be prevented. Furthermore, with the above-mentioned configuration, if it is used combining alkaline ink, the effectiveness that color bleeding can also be controlled will also do so.

[0175] In the above-mentioned ink for ink jets, it is desirable that the above-mentioned cationic



surface active agent is acetate of amines.

[0176] According to the above-mentioned configuration, by using the acetate of amines, the adjustment effectiveness of the surface tension of sufficient ink is acquired upwards, and the effectiveness that generating of a Kogation can be avoided much more certainly is done so.

[0177] In the above-mentioned ink for ink jets, it is desirable that the pH is adjusted within the limits of less than [ 4 or more ] seven.

[0178] If pH of ink is in the above-mentioned weak acidic condition according to the above-mentioned configuration, the effectiveness that the depressor effect of color bleeding can be raised further will be done so by combining with alkaline ink especially.

[0179] Moreover, the ink set for ink jets concerning this invention is a configuration containing the color ink which comes to contain the water soluble dye and the cationic surface active agent which have betaine structure in an aqueous solvent, and the black ink which shows alkalinity in an aqueous solvent, including a black pigment, in order to solve the above-mentioned technical problem.

[0180] While it is in the condition of black ink having been stabilized under alkaline conditions and having distributed the black pigment (suspension), first according to the above-mentioned configuration, color ink is in the condition that the water soluble dye which has betaine structure was stabilized under acid conditions. And a metal salt, the component in connection with gelation, etc. are hardly contained in each [ these ] ink. Therefore, even if these ink is heated with a nozzle, the effectiveness that generating of a Kogation is controlled is done so.

[0181] Moreover, if black ink and other color ink meet on a recorded material, alkaline black ink and acid color ink will cause an acid-alkaline reaction, and will precipitate easily [ a black pigment ] on a recorded material, and quickly taking advantage of this. Consequently, the effectiveness that generating of the color bleeding in a black pigment is controlled also does so.

[0182] Furthermore, since the above-mentioned black ink and color ink are in the condition of having been stabilized very much, even if they are a case so that the frequency of image formation may be small and the time amount between image formation actuation may be long, neither a black pigment nor water soluble dye solidifies, or they do not precipitate. Therefore, it also does so collectively the effectiveness that the outstanding shelf life can be demonstrated.

[0183] While pH of the above-mentioned color ink is within the limits of less than [ 4 or more ] seven, as for pH of the above-mentioned black ink, it is desirable that it is within the limits which becomes less than ten exceeding 7.

[0184] According to the above-mentioned configuration, since it will be adjusted to the range where pH of the both sides of black ink and color ink is desirable, the effectiveness that the above-mentioned acid-alkaline reaction can be generated much more effectively is done so.

[0185] In the above-mentioned ink set for ink jets, it is desirable that the black pigment contained in the above-mentioned black ink is an anion pigment.

[0186] According to the above-mentioned configuration, since a black pigment is an anion pigment, the effectiveness that the dispersibility of the black pigment in black ink can improve more, and can improve the shelf life of black ink further is done so. Moreover, by collapse of the balance of the ionic charge by the acid-alkaline reaction in black ink-color ink, since an anion pigment is condensed easily or precipitates, the effectiveness that it can control effectively also does so the color bleeding of the black ink in color picture formation collectively.

[0187] In the above-mentioned ink set for ink jets, it is desirable that either [ at least ] the dispersant which distributes a black pigment, or the binder which fixes a black pigment on a recorded material at the time of image formation is contained in the above-mentioned black ink.

[0188] According to the above-mentioned configuration, the dispersibility of a black pigment improves further by existence of a dispersant. Consequently, while raising the shelf life of black ink, the effectiveness that generating of a Kogation can be controlled further further is done so. Moreover, by existence of a binder, since fixing of a black pigment becomes quicker and certain, the effectiveness that generating of color bleeding can also be controlled further further is done so. If the both sides of the above-mentioned dispersant and a binder are included especially, while being able to raise the depressor effect of a Kogation and color bleeding more, the effectiveness that improvement in shelf-life nearby can be carried out is collectively done so.

[0189] The ink jet record approach concerning this invention is the approach of forming an image on

a recorded material using the ink set for ink jets mentioned above.

[0190] According to the above-mentioned approach, if black ink stable under alkaline conditions and color ink stable under acid conditions meet on a recorded material, black ink and color ink will cause an acid-alkaline reaction, and the balance of the ionic charge of black ink will fall. Therefore, the black pigment currently distributed to homogeneity precipitates very easily (or coagulation), and a black pigment precipitates easily and quickly on a recorded material. Consequently, a black pigment will be established without starting color bleeding, and does so the effectiveness that color bleeding can be controlled.

[0191] And since neither polyvalent metallic salt nor the component for gelation is included like before, while also being able to control generating of a Kogation, since it is in the condition that black ink and color ink were stabilized very much, the effectiveness that shelf life can also improve is done so.

[0192] Furthermore, since it is not necessary to adopt a configuration which carries out the regurgitation of polyvalent metallic salt and the ink separately, while being able to avoid complication and being able to low-cost-ize the configuration of an ink head, the effectiveness that the maintenance can also be simplified is done so.

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[Translation done.]

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**TECHNICAL FIELD**

[Field of the Invention] This invention relates to the ink for ink jets which makes high-definition image formation possible by controlling not only generating of color bleeding but generating of the so-called Kogation, and raising shelf life further especially, about the ink used for the image formation equipment of an ink jet method.

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**PRIOR ART**

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[Description of the Prior Art] The thing of various methods is proposed and put in practical use as image formation equipment for hard copy. Especially, the image formation equipment (ink jet printer) of an ink jet method (drop injection recording method) is preferably used for the application which forms a high-definition color picture in it especially since the cost of the whole equipment can be low held down to the top in which high-definition image formation is possible.

[0003] Here, in the above-mentioned ink jet method, it is known that the trouble called color bleeding or bleeding will occur conventionally.

[0004] That is, by the ink jet method, in order to obtain a color picture, the ink of two or more colors which use water as the main solvent is usually recorded in piles on recorded materials, such as paper. Before the ink of a certain color previously breathed out on the recorded material is established at this time, the ink of other colors will be breathed out one after another, and it will pile up. Therefore, in the part used as the boundary of a different color, the phenomenon, i.e., color bleeding, in which the ink of a different color is spread, or move and the boundary line of each color becomes indefinite, or bleeding (it unifies with color bleeding hereafter) occurs.

[0005] If the above-mentioned color bleeding occurs, since a blot arises between different colors or each color will be in the condition of having been mixed with the ununiformity, image grace is reduced. When color bleeding arises between this black and other colors, the boundary of the image of black bleeds, or it fades, and image grace is made to fall very much especially, although black serves as most important color in image formation.

[0006] Then, the technique which controls generating of this color bleeding is variously proposed from the former. For example, the technique which controls color bleeding is indicated by JP,5-202328,A and JP,6-106375,A by using polyvalent metallic salt for the coagulation of ink.

[0007] By JP,5-202328,A, after supplying a polyvalent-metallic-salt solution on a recorded material previously using the ink containing the color which has at least one carboxyl group, and polyvalent metallic salt, specifically, ink is supplied. While ink dries quickly on a recorded material and generating of color bleeding is controlled by this, the water resisting property of the ink after desiccation can also be raised.

[0008] Moreover, in JP,6-106735,A, each ink of yellow, a Magenta, and cyanogen contains the surface active agent or permeability solvent which gives permeability, and the salt, and the ink of black contains the component which causes thickening or condensation by operation of the above-mentioned salt. By this, while controlling generating of color bleeding, the homogeneity of image concentration can be raised and the grace of black can be raised further.

[0009] Furthermore, in JP,8-209049,A, the technique using the 2nd constituent including the gelation initiation kind which reacts with the 1st constituent including a gel formation kind and this 1st constituent, and forms gel is indicated. With this technique, generating of color bleeding is controlled by making gel form in the field which adjoins the class product between discharge and each field.

[0010] Moreover, in addition to using the above-mentioned polyvalent metallic salt, in JP,9-207424,A, the technique of making ink containing a pigment and a resin emulsion is indicated. By the interaction with polyvalent metal ion, the above-mentioned resin emulsion controls osmosis of a coloring component, and promotes fixing to a recorded material. Moreover, a resin emulsion can form a coat on a recorded material, and can also raise the scuff resistance of printed matter. If a pigment is

furthermore used, it will become possible to control osmosis of the coloring component in ink more. Color bleeding is controlled further further by such operation.

[0011] In addition, in JP,11-349878,A, the interaction of ion is produced between black ink and color ink, and the technique which controls color bleeding is indicated. While making black ink contain an anion pigment, color ink is made to contain the component (for example, a cationic surface active agent and a cation salt) which supplies a cation with this technique. Consequently, the interaction of the ion between black ink-color ink arises, and generating of color bleeding is controlled.

[0012] By the way, it is also known that the trouble which heats ink at the heater in a nozzle in an instant, and is called [ by the pressure of the generated air bubbles ] a Kogation also in the above-mentioned ink jet method in the thermal jet method which makes ink breathe out in addition to the above-mentioned color bleeding from a nozzle will occur.

[0013] Generally the inorganic impurity of the matter produced by the pyrolysis of the coloring component in ink and the minute amount contained in ink, an aggregate, etc. adhere and deposit a Kogation on the above-mentioned heater, and it means the phenomenon [ the regurgitation of the ink by which it becomes impossible for ink heating at a heater to fully have carried out, and it was stabilized as a result ] no longer maintaining. It is known that the inorganic ion in ink (especially metal ion) will have big effect on generating of this Kogation especially.

[0014] For example, when the cation salt is contained in the presentation of ink, by heating on a heater the inorganic ion which forms this cation salt, it reacts with other presentations of ink and insoluble matter may be formed. If such insoluble matter adheres and deposits on a heater, the above-mentioned Kogation will occur.

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## EFFECT OF THE INVENTION

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Since it becomes impossible to demonstrate (namely, the adjustment effectiveness of the surface tension mentioned later), it is not desirable.

[0079] Moreover, as an example of quarternary ammonium salt, poly propoxy quarternary ammonium salt, such as the 4th class ammonium acetate of poly propoxy and the 4th class ammonium chloride of poly propoxy, is used preferably, for example. Each these poly propoxy quarternary ammonium salt is WITCO Corporation. Emcol It is marketed as series etc.

[0080] As an example of the counter ion which can be combined with the above-mentioned cationic surface active agent, acetic-acid ion, formic-acid ion, chloride ion, gluconic-acid ion, succinic-acid ion, tartaric-acid ion, glutaric-acid ion, malonic-acid ion, carboxylic-acid ion, fumaric-acid ion, malic-acid ion, sebacic-acid ion, adipic-acid ion, stearin acid ion, oleic acid ion, lauric-acid ion, benzoic-acid ion, citric-acid ion, etc. are mentioned. Especially, as mentioned above, acetic-acid ion and chloride ion are desirable, and acetic-acid ion is much more desirable.

[0081] The above-mentioned cationic surface active agent is added in order to adjust the surface tension of color ink. It is more desirable to exist in this color ink by the concentration of about 0.5 - 5% of the weight of within the limits, and to have about 3% of the weight of concentration as the concrete content. By containing the cationic surface active agent within the limits of this, it becomes possible to adjust the wettability on the orifice in the head of thermal jet, or a recorded material (paper) good.

[0082] If the content of the above-mentioned cationic surface active agent is less than about 0.5 % of the weight, since the adjustment effectiveness of sufficient surface tension is not acquired, it is not desirable. On the other hand, if it exceeds about 5 % of the weight, since the adjustment effectiveness of surface tension of having balanced the addition will not be acquired upwards, viscosity etc. will become high and the function as color ink will fall, it is not desirable.

[0083] The color ink concerning this invention which comes to contain the water soluble dye which has the above-mentioned betaine structure, and a cationic surface active agent shows acidity, within the limits (it is  $4 \leq \text{pHCl} < 7$  when pH of color ink is set to pHCl) of less than [ 4 or more ] seven has desirable pH, and, specifically, within the limits ( $6 \leq \text{pHCl} < 7$ ) of less than [ 6 or more ] seven has more desirable pH. That is, as for the above-mentioned color ink, it is more desirable that the acescence is shown. Although the color ink applied to this invention by addition of the above-mentioned cationic surface active agent will show the acescence, if acetate and quarternary ammonium salt of amines are especially used as a cationic surface active agent, it can adjust pH within the limits of [ six or more / more desirable ] less than seven.

[0084] In addition, in order to adjust ink to acidity, pH regulator (a buffer/buffer) may be added. However, in the color ink concerning this invention, what contains a metal salt as a pH regulator cannot be used from the need of avoiding generating of a Kogation.

[0085] As an aquosity solvent contained in the color ink concerning this invention, it comes to contain other still more nearly meltable solvents in water including water at least. Inorganic ion which causes a Kogation is not contained as the above-mentioned water, but although it is not limited especially if it has the purity of extent generally used as an object for ink, ion exchange water (deionized water) is used preferably.

[0086] As a content of the water in color ink, when color ink all weight is made into 100 % of the

weight, it is desirable that it is 10 – 90% of the weight of within the limits, and is 30 – 80% of the weight of within the limits, and it is more desirable that it is 50 – 95% of the weight of within the limits.

[0087] It will not be limited especially if the operation of control of generating of the various operations in color ink, i.e., desiccation of ink, coloring or the Kogation in this invention, or color bleeding is not checked as other solvents meltable in the above-mentioned water.

[0088] Specifically as a solvent besides the above, they are a methanol, ethanol, n-propanol, and isopropanol (2-propanol), n-butanol, a sec-butanol, a tert-butanol, an iso-butanol, Alkyl alcohols of the carbon numbers 1–5, such as n-pentanol; Dimethylformamide, Amides, such as dimethylacetamide; Ketones, such as an acetone and diacetone alcohol, or a keto alcohol; tetrahydrofuran, Ether, such as dioxane; Oxypropylene copolymer (polyalkylene glycols); polyethyleneimine; ethylene glycol, such as a polyethylene glycol and a polypropylene glycol, Propylene glycol, a butylene glycol, a trimethylene glycol, Triethylene glycol, 1 and 2, 6-hexane triol, a thioglycol, Hexylene glycol, a diethylene glycol, tetraethylene glycol, Dipropylene glycol, tripropylene glycol, 1,5-pentanediol, Polyhydric alcohol, such as a glycerol; Ethylene glycol monomethyl ether, Ethylene glycol monoethyl ether, the diethylene-glycol monomethyl ether, Diethylene glycol monoethyl ether, the diethylene-glycol monobutyl ether, The low-grade monoalkyl ether of polyhydric alcohol, such as the triethylene glycol monomethyl ether and the triethylene glycol monoethyl ether, Triethylene glycol wood ether, Triethylene glycol diethylether, tetraethylene glycol wood ether, low-grade dialkyl ether [ of polyhydric alcohol, such as tetraethylene glycol diethylether, ]; — trimethylol propane; — monoethanolamine — Organic amines, such as diethanolamine, triethanolamine, 2-pyrrolidone, a N-methyl-2-pyrrolidone, 1,3-dimethyl-2-imidazolidinone, and a sulfolane; various kinds of water-soluble organic solvents urea; etc. are mentioned. The water-soluble above-mentioned organic solvent may be used independently, and may be used also as two or more kinds of mixture.

[0089] Also in the water-soluble above-mentioned organic solvent, the low-grade alkyl ether of polyhydric alcohol, such as polyhydric alcohol, such as alcohol of monovalence, such as iso-propanol (2-propanol), a diethylene glycol, and 1,5-pentanediol, the triethylene glycol monomethyl (or ethyl) ether, and the diethylene-glycol monobutyl ether, trimethylol propane, etc. are desirable especially. Since the alcohol of monovalence is a low-boiling point, the effectiveness of shortening the drying time of color ink at the time of image formation is acquired. Moreover, since the low-grade alkyl ether of polyhydric alcohol or polyhydric alcohol is a high-boiling point, it functions as a wetting agent which controls the desiccation which is not desirable as for color ink.

[0090] Although it is not limited, when color ink all weight is made into 100 % of the weight, especially the content of the water-soluble above-mentioned organic solvent contained in the color ink concerning this invention has 3 – 50% of the weight of desirable within the limits, and 3 – 40% of the weight of its within the limits is more desirable.

[0091] Moreover, when dividing the water-soluble above-mentioned organic solvent into the thing of a low-boiling point, and the thing of a high-boiling point and adding, when color ink is made into 100 % of the weight, in the case of a low-boiling point organic solvent, 0.5 – 10% of the weight of within the limits is desirable, and 1.5 – 6% of the weight of within the limits is more desirable [ in the case of ]. Moreover, when color ink is made into 100 % of the weight, in the case of a high-boiling point organic solvent, 0.5 – 40% of the weight of within the limits is desirable, and it is more desirable. [ of 2 – 20% of the weight of within the limits ]

[0092] In addition, each range where the content of the water-soluble organic solvent mentioned above is desirable shall be included, also when each water-soluble organic solvent is used independently, and also when it uses as two or more kinds of mixture. namely, the above — the desirable range is desirable range as a total content of a water-soluble organic solvent.

[0093] Moreover, in order to acquire a desired physical-properties value, the color ink concerning this invention can attach a defoaming agent, antiseptics, an antifungal agent, etc. other than the component mentioned above if needed, and can add the water soluble dye of other marketing etc. further. About examples and additions, such as these defoaming agents, antiseptics, and an antifungal agent, it is not limited especially unless it has a bad influence on many properties of color ink, and a well-known technique can be used suitably conventionally.

[0094] In the ink set for ink jets concerning this invention, the black ink in which the presentation

which contains a black pigment in an aqueous solvent is made indispensable in addition to the color ink containing each above-mentioned component, and alkalinity is shown is included.

[0095] Although the carbon black generally used for black ink can be mentioned as a black pigment contained in the above-mentioned black ink and it is not limited especially, especially the anion pigment charged in anionic is desirable in a water solution by embellishing a carboxyl group on the surface of a black pigment especially.

[0096] The method of obtaining the carbon black which introduced  $\text{-COONa}$  (sodium salt of a carboxyl group) on the surface of carbon black, and was charged in anionic as a concrete example of this anion pigment is mentioned. After often mixing in water and making it distribute acid commercial carbon black, a sodium hypochlorite is specifically dropped and heated to this, the obtained slurry is filtered and rinsed after that and a pigment wet cake is obtained, further, water is made to re-distribute this and it desalts by the reverse osmotic membrane, and although the method of condensing these pigment dispersion liquid is mentioned further, it is not limited especially.

[0097] Furthermore, it is also possible to use commercial self-distributed carbon black as an anion pigment. For example, the self-distributed carbon black "KYABO jet" (a trade name, Cabot make) which the carboxyl group ( $\text{-COO-}$ ) coupled directly and was charged in anionic is mentioned.

[0098] It is very desirable that the dispersant for distributing a black pigment is contained in the above-mentioned black ink. When using especially carbon black which is not self-distributed process input output equipment, it is very desirable that a dispersant is added from the point which avoids precipitate of this carbon black and raises shelf life.

[0099] Specifically as this dispersant, the various resin which has a carboxyl group can be mentioned. If the various resin which has such a carboxyl group is added as a dispersant, as for black ink, alkalinity will be shown and a black pigment, especially an anion pigment will serve as a stable solution (dispersion liquid/suspension) under these conditions. Consequently, even if it leaves it for a long period of time, a pigment precipitating or solidifying is controlled and it can acquire the outstanding shelf life.

[0100] As various resin which has the above-mentioned carboxyl group, a styrene-acrylic-acid copolymer, a styrene-acrylic-acid-acrylic-acid alkyl ester copolymer, a styrene-maleic-acid copolymer, a styrene-maleic-acid-acrylic-acid alkyl ester copolymer, a styrene-methacrylic-acid copolymer, a styrene-methacrylic-acid-acrylic-acid alkyl ester copolymer, a styrene-maleic-acid half ester copolymer, a vinyl naphthalene-acrylic-acid copolymer, vinyl naphthalene-maleic-acid copolymers, or these salts are mentioned, for example. Especially, styrene-acrylic resin is desirable and especially a styrene-acrylic-acid copolymer is desirable.

[0101] When the whole black ink is made into 100 % of the weight, as for various kinds of above-mentioned resin, it is desirable to contain by 0.1 - 5% of the weight of within the limits, and it is more desirable to contain by 0.3 - 2% of the weight of within the limits.

[0102] In addition, a thing usable also as a binder mentioned later is also contained in various kinds of above-mentioned resin. In that case, since the number of components added by black ink decreases, preparation of black ink can be simplified.

[0103] Moreover, as the above-mentioned dispersant, a resin emulsion is mentioned to others. A continuous phase is water and the resin emulsion said here means the emulsion whose dispersed phases are the following resinous principles.

[0104] As a resinous principle of the dispersed phase in the above-mentioned resin emulsion, acrylic resin, vinyl acetate system resin, styrene-butadiene resins, vinyl chloride system resin, acrylic-styrene resin, butadiene system resin, styrene resin, bridge formation acrylic resin, bridge formation styrene resin, benzoguanamine resin, phenol resin, silicone resin, an epoxy resin, etc. are mentioned.

[0105] The above-mentioned resin emulsion can be obtained by carrying out the distributed polymerization (emulsion polymerization) of the resin monomer underwater with a surfactant according to a situation. For example, the emulsion of acrylic resin or styrene-acrylic resin is obtained by carrying out the distributed polymerization of acrylic ester (meta) or (meta) acrylic ester, and the styrene underwater with a surfactant.

[0106] the rate of the resin as the above-mentioned dispersed phase component, and water — the resin 100 weight section — receiving — water 60 — the 400 weight sections — within the limits of the 100 - 200 weight section is preferably suitable.



[0107] Moreover, it is also possible to use a commercial resin emulsion. As a commercial resin emulsion, it is the micro gel E-1002 and E-5002 (a styrene-acrylic resin emulsion, Nippon Paint Co., Ltd. make), for example, BONKOTO 4001 (an acrylic resin emulsion, Dainippon Ink & Chemicals, Inc. make), BONKOTO 5454 (a styrene-acrylic resin emulsion, Dainippon Ink & Chemicals, Inc. make), SAE-1014 (a styrene-acrylic resin emulsion, Nippon Zeon Co., Ltd. make), SAIBI Norian SK-200 (an acrylic resin emulsion, SAIDEN CHEMICAL INDUSTRY CO., LTD. make), etc. are mentioned.

[0108] When the above-mentioned resin emulsion makes black ink 100 % of the weight at this invention, it is desirable to be contained at 0.1 - 40% of the weight of within the limits, and it is more desirable to be contained at 1 - 25% of the weight of within the limits.

[0109] Moreover, as a dispersant in this invention, both the resin which has the above-mentioned carboxyl group, and the above-mentioned resin emulsion may be contained. Furthermore, when a black pigment is an anion pigment with high dispersibility, the dispersant does not necessarily need to be contained.

[0110] Furthermore, the binder which fixes a black pigment on a recorded material at the time of image formation may be contained in the above-mentioned black ink. As this binder \*\*, for example, polyurethane resin, starch, gelatin, a latex, Water soluble polymers, such as casein, gum arabic, sodium alginate, and polyacrylamide; Methyl cellulose, Cellulosics, such as a carboxy cellulose and a hydroxymethyl cellulose; Polyacrylate, A vinyl naphthalene-acrylic-acid copolymer, a styrene-maleic-acid copolymer, and its salt, Anionic (anion nature) giant molecules, such as sodium salt of beta-naphthalene sulfonic-acid formalin condensation product, and phosphate; the Nonion nature (nonionic) giant molecules, such as polyvinyl alcohol, a polyvinyl pyrrolidone, and a polyethylene glycol, etc. are mentioned.

[0111] When black ink is made into 100 % of the weight, as for the content of the above-mentioned binder, it is desirable to contain by 0.5 - 30% of the weight of within the limits. If it is less than 0.5 % of the weight, the effectiveness by adding a binder will not be acquired. On the other hand, if it exceeds 30 % of the weight, since the effectiveness corresponding to an addition will not be acquired upwards, viscosity etc. will become high and the function as black ink will fall, it is not desirable.

[0112] It comes to contain other still more nearly meltable solvents in water including water at least like the color ink mentioned above as an aqueous solvent contained in the above-mentioned black ink. Since it is the same as that of the water-soluble organic solvent illustrated by explanation of the color ink which each mentioned above also as other solvents also as the above-mentioned water, the detailed explanation is omitted.

[0113] The above-mentioned black ink has desirable within the limits (it is  $7 < \text{pHBk} \leq 10$  when pH of black ink is set to pHBk) from which it indicates that alkalinity mentioned above, and pH exceeds 7 and specifically becomes ten or less, and its within the limits ( $7 < \text{pHBk} \leq 9$ ) which pH exceeds 7 and becomes nine or less is more desirable. That is, as for the above-mentioned black ink, it is more desirable that alkalescence is shown.

[0114] It is very desirable that organic amines, such as 2-pyrrolidone, are contained in the above-mentioned black ink also in the water-soluble organic solvent mentioned above here, for example. While these organic amines function as a pH regulator (a buffer/buffer) which adjusts black ink to alkalescence, a Kogation is preferably used, in order not to cause. Moreover, when black ink is made into 100 % of the weight, as for the content, it is desirable to contain by 0.001 - 10% of the weight of within the limits.

[0115] Moreover, in order to acquire a desired physical-properties value, the black ink concerning this invention can attach a defoaming agent, antiseptics, an antifungal agent, etc. other than the component mentioned above if needed, and can add the water soluble dye of other marketing etc. further. About examples and additions, such as these defoaming agents, antiseptics, and an antifungal agent, it is not limited especially unless it has a bad influence on many properties of black ink, and a well-known technique can be used suitably conventionally.

[0116] The ink set containing the color ink, and this color ink and the above-mentioned black ink as ink for ink jets concerning this invention concerning this invention is widely applicable to various well-known ink jet printers conventionally.

[0117] As a typical method of the above-mentioned ink jet printer, the piezo jet method which carries out the regurgitation of the ink in a nozzle according to physical deformation of a piezo-electric

element, and the thermal jet method which carries out the regurgitation with the air bubbles which apply heat to the ink in a nozzle and are generated are held. the ink set concerning this invention — the above — although it can use suitable for any method, it is especially used for the thermal jet method which a Kogation tends to generate by heating ink especially preferably.

[0118] In the above-mentioned ink jet recording method, the above-mentioned black ink and color ink are separately breathed out from the nozzle of a head, respectively, and contact mutually by forming an image in the paper as a recorded material.

[0119] Here, especially at the former, the phenomenon, i.e., color bleeding, in which each ink is spread, or move and the boundary line of each color becomes indefinite occurs in the part used as black and a boundary with other colors. Consequently, the boundary of the image of black bleeds, or it fades, and image grace is made to have been to fall very much especially.

[0120] Moreover, the ink component adhered to the heater part of a nozzle from the problem on the presentation of ink, produced the Kogation, or when the frequency of image formation was small and the time amount between image formation actuation was long, the color and pigment of ink solidified, or it precipitated, the nozzle was got blocked, and the trouble that shelf life also fell was invited.

[0121] On the other hand, in this invention, first, within a head, while it is in the condition of black ink having been stabilized under alkaline conditions and having distributed the black pigment (suspension), color ink is in the condition that the water soluble dye which has betaine structure was stabilized under acid conditions. And a metal salt, the component in connection with gelation, etc. are hardly contained in each [ these ] ink. Therefore, even if it is a case so that a Kogation may not be produced even if heated with a nozzle, and the frequency of image formation may be small and the time amount between image formation actuation may be long, neither a black pigment nor water soluble dye solidifies, or it does not precipitate.

[0122] Furthermore, if black ink and other color ink meet on a recorded material, alkaline black ink and acid color ink will cause an acid-alkaline reaction, and the balance of the ionic charge of black ink will fall. In black ink, in the condition with the good charge balance of ion, although the black pigment is distributing to homogeneity, if the balance falls, since it will become easy to precipitate very easily (or coagulation), a black pigment precipitates easily on a recorded material, and quickly. Consequently, a black pigment will be established without starting color bleeding, and can control color bleeding.

[0123] The inhibition mechanism of the above-mentioned color bleeding is explained more concretely. For example, suppose that color ink contains the water soluble dye of betaine structure, and a cationic surface active agent noting that black ink contains an anion pigment as a black pigment and contains styrene-acrylic resin as a dispersant.

[0124] If these are separately breathed out from a nozzle and meet on a recorded agent, the styrene-acrylic resin which is the dispersant which was distributing the anion pigment good, and the cationic surface active agent of color ink will cause an acid-alkaline reaction. Namely, the carboxyl group in the end of styrene-acrylic resin and the cation which shows the surface activity effectiveness in a cationic surface active agent react, and the ionic charge balance in black ink becomes unstable by making this reaction into a driving force. By this, while an anion pigment precipitates easily, it also solidifies easily the above-mentioned styrene-acrylic resin which was being distributed in black ink.

[0125] Consequently, it solidifies and condenses certainly, without styrene-acrylic resin's making the precipitating anion pigment established, and black ink's not carrying out osmosis to a recorded material, either, but generating color bleeding between color ink.

[0126] Thus, by the ink jet recording method concerning this invention, the fixing reaction of the black which makes an acid-alkaline reaction a driving force on a recorded material is produced by using alkaline black ink and acid color ink. Consequently, color bleeding is controlled certainly.

[0127] And even if it is the ink jet printer of a thermal jet method, it is not made to produce a Kogation especially, since a component which is concerned with a metal salt or a gelation reaction is not contained in each above-mentioned ink. Furthermore, in order to make color bleeding control, if each above-mentioned ink is original, it shows the acidity or alkalinity which is in a condition unstable as ink. However, since the pigment is distributed good with anion-izing and a dispersant while betaine-izing water soluble dye, even if it leaves it for a long period of time, an ink component can

solidify, or cannot precipitate, but the trouble that the image formation of the nozzle cannot be got blocked and carried out can also be avoided. Consequently, it is that whose shelf life of ink also improved very much.

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[Translation done.]

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**TECHNICAL PROBLEM**

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[Problem(s) to be Solved by the Invention] Here, in the Prior art mentioned above, avoiding generating of the above-mentioned Kogation of what can control color bleeding to some extent has invited the trouble of being difficult.

[0016] The ion of this polyvalent metallic salt generates a Kogation, and it stops first, being able to carry out the regurgitation of the ink from a head normally with the technique of using polyvalent metallic salt for the coagulation of ink. Therefore, with each technique of above-mentioned JP,5-202328,A, JP,6-106375,A, and JP,9-207424,A, the reaction mixture and ink containing polyvalent metallic salt are separately breathed out on a recorded material (paper), respectively, and reaction mixture and ink are mixed on this recorded material. However, with the technique which carries out the regurgitation of two kinds of components separately in this way, the structure of an ink head becomes complicated, a manufacturing cost is raised upwards and the trouble of also making control and a maintenance of image formation make it complicated is invited.

[0017] On the other hand, since the combination of the gel formation kind included in the 1st-2nd constituent or a gelation initiation kind becomes the cause of generating a Kogation, in JP,8-209049,A, the trouble that practicality is missing applying to a thermal jet method too is invited.

[0018] Furthermore, in JP,11-349878,A, most matter used as the factor which generates the Kogation of polyvalent metallic salt, the gel formation kind, the gelation initiation kind, etc. which were mentioned above is not included. Therefore, the theory top is possible for generating of color bleeding controlling generating of a Kogation. However, it is indispensable to use a cation salt or a cationic surface active agent with this technique. Although these matter is stable under acid conditions, since the unnecessary matter will be generated in water and effect will be lost if alkali etc. is blended, ink must show acidity.

[0019] When ink shows acidity, the color and pigment which are contained as a color component will be solidified, will become easy to precipitate, consequently will usually produce a big problem at the shelf life and stability of ink. Thus, if the shelf life and stability of ink fall, possibility that coagulation and precipitate will arise within the head of thermal jet at the time of image formation cannot become high, either, and cannot control generating of a Kogation certainly as a result.

[0020] Furthermore, with the technique of above-mentioned JP,11-349878,A, although it is describing adjusting pH in order to optimize many properties of ink, about the range of concrete pH, reference is not made at all. Therefore, in the above-mentioned technique, concrete measures are not taken at all about the fall of the shelf life by coagulation or precipitate of a color or a pigment.

[0021] Generally, the sulfonic group and the carboxyl group are contained in most colors and pigments. Therefore, if a cationic surface active agent and a cation salt are added to the ink containing these colors or a pigment, an aggregate will produce [ the above-mentioned sulfonic group, a carboxyl group, and a cationic surface active agent or a cation salt ] an acid-alkaline reaction in a lifting and ink easily. Therefore, the ink containing the above-mentioned cationic surface active agent, a cation salt, etc. serves as a presentation which an aggregate tends to generate according to an acid-alkaline reaction.

[0022] It is not only easy to generate an aggregate in ink, but in such ink, condensation significant work increases with the passage of time, or size becomes large. Therefore, in order that an aggregate occurs, and it becomes easy to get it blocked to leave it for a long period of time in the ink passage

in an ink cartridge, and it bars the regurgitation of ink upwards, and this aggregate may adhere and accumulate and may cause a Kogation on the above-mentioned heater, heating by which the ink at a heater was stabilized is barred and the regurgitation of ink becomes unstable.

[0023] That is, the ink of the presentation containing a cationic surface active agent or a cation salt not only tends to cause a Kogation, but since an aggregate occurs with time, the shelf life of ink will fall. Consequently, finally, the regurgitation capacity of ink declines irreversibly and invites the trouble that the life of an ink cartridge is also shortened.

[0024] It is in this invention being made in view of the above-mentioned trouble, and the purpose controlling generating of color bleeding or a Kogation certainly, and also raising shelf life, avoiding complication of the configuration of an ink head further, and offering the ink for ink jets which can be used suitable for the image formation equipment of a thermal jet method.

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**MEANS**

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[Means for Solving the Problem] As a result of inquiring wholeheartedly in view of the above-mentioned trouble, while this invention persons produce the interaction of ion between color ink and black ink By using what has betaine structure at the end as a color contained in the ink used as color ink It came to complete a header and this invention for it being possible to be able to control not only color bleeding but generating of a Kogation upwards, and to also raise shelf life.

[0026] That is, the ink for ink jets concerning this invention is characterized by coming to contain the water soluble dye which has betaine structure, and a cationic surface active agent in an aquosity solvent, in order to solve the above-mentioned technical problem.

[0027] Usually, according to the above-mentioned configuration, although the trouble which the above-mentioned ink serves as acidity and water soluble dye solidifies occurs under conditions with a cationic surface active agent, since the above-mentioned water soluble dye has betaine structure, also under acid conditions, it will be in the condition of having been stabilized very much, and the shelf life of ink will improve. And a metal salt, the component in connection with gelation, etc. are hardly contained in the above-mentioned ink. Therefore, even if heated with a nozzle, a Kogation is hardly produced. Furthermore, with the above-mentioned configuration, if it is used combining alkaline ink, color bleeding can also be controlled.

[0028] In the above-mentioned ink for ink jets, it is desirable that the above-mentioned cationic surface active agent is acetate of amines.

[0029] According to the above-mentioned configuration, by using the acetate of amines, the adjustment effectiveness of the surface tension of sufficient ink is acquired upwards, and generating of a Kogation can be avoided much more certainly.

[0030] In the above-mentioned ink for ink jets, it is desirable that the pH is adjusted within the limits of less than [ 4 or more ] seven.

[0031] If it is in the condition, i.e., a weak acidic condition, that pH of ink was adjusted to above-mentioned within the limits according to the above-mentioned configuration, the depressor effect of color bleeding can be further raised by combining with alkaline ink especially.

[0032] Moreover, the ink set for ink jets concerning this invention is characterized by including the color ink which comes to contain the water soluble dye and the cationic surface active agent which have betaine structure in an aquosity solvent, and the black ink in which alkalinity is shown in an aquosity solvent, including a black pigment, in order to solve the above-mentioned technical problem.

[0033] While it is in the condition of black ink having been stabilized under alkaline conditions and having distributed the black pigment (suspension), first according to the above-mentioned configuration, color ink is in the condition that the water soluble dye which has betaine structure was stabilized under acid conditions. And a metal salt, the component in connection with gelation, etc. are hardly contained in each [ these ] ink. Therefore, generating of a Kogation is controlled even if these ink is heated with a nozzle.

[0034] Moreover, if black ink and other color ink meet on a recorded material, alkaline black ink and acid color ink will cause an acid-alkaline reaction, and will precipitate easily [ a black pigment ] on a recorded material, and quickly taking advantage of this. Consequently, a black pigment is established, without starting color bleeding.

[0035] Furthermore, since the above-mentioned black ink and color ink are in the condition of having

been stabilized very much, even if they are a case so that the frequency of image formation may be small and the time amount between image formation actuation may be long, neither a black pigment nor water soluble dye solidifies, or they do not precipitate. Therefore, the outstanding shelf life can be demonstrated.

[0036] While pH of the above-mentioned color ink is within the limits of less than [ 4 or more ] seven, as for pH of the above-mentioned black ink, it is desirable that it is within the limits which becomes less than ten exceeding 7.

[0037] According to the above-mentioned configuration, since it will be adjusted to the range where pH of the both sides of black ink and color ink is desirable, the above-mentioned acid-alkaline reaction can be generated much more effectively.

[0038] In the above-mentioned ink set for ink jets, it is desirable that the black pigment contained in the above-mentioned black ink is an anion pigment.

[0039] According to the above-mentioned configuration, since a black pigment is an anion pigment, the dispersibility of the black pigment in black ink improves more. Consequently, the shelf life of black ink can be improved further. Moreover, in order to depend for the distributed condition of an anion pigment on the balance of the ionic charge in black ink greatly, when the balance of ionic charge collapses according to the acid-alkaline reaction in black ink-color ink, an anion pigment will be condensed easily or will precipitate. Therefore, the color bleeding of the black ink in color picture formation can be controlled effectively.

[0040] In the above-mentioned ink set for ink jets, it is desirable that either [ at least ] the dispersant which distributes a black pigment, or the binder which fixes a black pigment on a recorded material at the time of image formation is contained in the above-mentioned black ink.

[0041] According to the above-mentioned configuration, the dispersibility of a black pigment improves further by existence of a dispersant. Consequently, while raising the shelf life of black ink, generating of a Kogation can be controlled further further. Moreover, by existence of a binder, since fixing of a black pigment becomes quicker and certain, generating of color bleeding can also be controlled further further. If the both sides of the above-mentioned dispersant and a binder are included especially, while being able to raise the depressor effect of a Kogation and color bleeding more, improvement in shelf-life nearby can be carried out.

[0042] The ink jet record approach concerning this invention is characterized by forming an image on a recorded material using the ink set for ink jets mentioned above.

[0043] According to the above-mentioned approach, if black ink stable under alkaline conditions and color ink stable under acid conditions meet on a recorded material, black ink and color ink will cause an acid-alkaline reaction, and the balance of the ionic charge of black ink will fall. Therefore, the black pigment currently distributed to homogeneity precipitates very easily (or coagulation), and a black pigment precipitates easily and quickly on a recorded material. Consequently, a black pigment will be established without starting color bleeding, and can control color bleeding.

[0044] And since neither polyvalent metallic salt nor the component for gelation is included like before, while also being able to control generating of a Kogation, since it is in the condition that black ink and color ink were stabilized very much, shelf life will also improve. Furthermore, the maintenance can also be simplified, while being able to avoid complication and being able to low-cost-ize the configuration of an ink head, since it is not necessary to adopt a configuration which carries out the regurgitation of polyvalent metallic salt and the ink separately.

[0045]

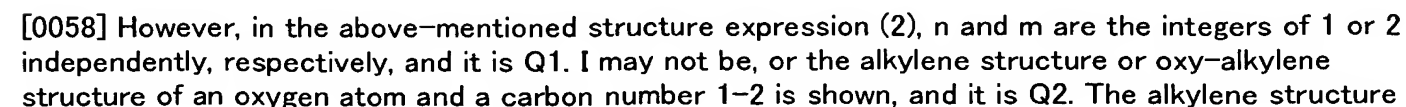
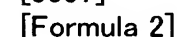
[Embodiment of the Invention] It will be as follows if one gestalt of operation of this invention is explained. In addition, this invention is not limited to this.

[0046] Especially the ink for ink jets concerning this invention is suitably used as color ink for color picture formation, and comes to contain the water soluble dye which has betaine structure in an aqueous solvent, and a cationic surface active agent. Therefore, a high-definition image can be formed good, controlling generating of color bleeding and a Kogation and demonstrating high shelf life.

[0047] Moreover, while the ink set concerning this invention is ink in which the presentation in which this black ink contains a black pigment in an aqueous solvent is made indispensable, and alkalinity is shown coming [ at least one kind of color ink, and one kind of black ink ], the above-mentioned color



[Formula 1]





or oxy-alkylene structure of carbon numbers 1-4 is shown, and D shows an oxygen atom and the alkylene structure of a carbon number 1-2.

[0059] As a suitable example of water soluble dye expressed with the above-mentioned basic structure X As a color of yellow, the acid yellow 23, the direct yellow 86, etc. for example, as a color of a Magenta The reactive red 58, the reactive red 120, the reactive red 180, acid red 52, acid red 214, etc. as a color of cyanogen Although the acid blue 7, the acid blue 9, the direct blue 86, the direct blue 199, etc. are mentioned, it is not limited especially and well-known water soluble dye can be conventionally chosen suitably according to a color to make it color as color ink.

[0060] The above-mentioned intramolecular acidic group B - Although it is not limited especially if it is the atomic group which shows acidity, a sulfonic group ( $-\text{SO}_3-$ ) and a carboxyl group ( $-\text{COO}-$ ) can be mentioned preferably, for example.

[0061] Above R1 Or R2 As an alkyl group of the carbon numbers 1-4 shown, a methyl group ( $\text{CH}_3-$ ), an ethyl group ( $\text{C}_2\text{H}_5-$ ), a propyl group ( $\text{C}_3\text{H}_7-$ ), butyl ( $\text{C}_4\text{H}_9-$ ), and an isopropyl group ( $\text{CH}_3$ ) ( $2\text{CH}-$ ) are mentioned, for example.

[0062] Above Q1 As alkylene structure of the carbon number 1-2 shown, methylene ( $-\text{CH}_2-$ ) and ethylene ( $-\text{C}_2\text{H}_4-$ ) are mentioned, and oxy-methylene ( $-\text{OCH}_2-$ ) and oxyethylene ( $-\text{OC}_2\text{H}_4-$ ) are mentioned as oxy-alkylene structure. Moreover, the above Q2 As alkylene structure of the carbon numbers 1-4 shown Methylene ( $-\text{CH}_2-$ ), ethylene ( $-\text{C}_2\text{H}_4-$ ), trimethylene ( $-\text{C}_3\text{H}_6-$ ), Tetramethylen ( $-\text{C}_4\text{H}_8-$ ) is mentioned. As oxy-alkylene structure Oxy-methylene ( $-\text{OCH}_2-$ ), oxyethylene ( $-\text{OC}_2\text{H}_4-$ ), oxy-trimethylene ( $-\text{OC}_3\text{H}_6-$ ), and oxy-tetramethylen ( $-\text{OC}_4\text{H}_8-$ ) are mentioned.

[0063] As alkylene structure of the carbon number 1-2 shown by Above D, each structure of the above-mentioned methylene and ethylene is mentioned. Since an oxygen atom is sufficient as this D, specifically as a nitrogen-containing monocycle type heterocyclic compound in the above-mentioned structure expression (2), a pyrrolidine, a piperidine, hexamethyleneimine, a morpholine, etc. are mentioned.

[0064] In addition, in this invention, although the most general 4th class ammonium structure as an inner salt machine nature machine was mentioned as the example in the above-mentioned example, if the above-mentioned betaine structure can be formed, it cannot be overemphasized that inner salt machine nature machines may be other base structures.

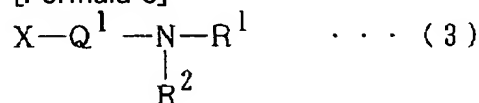
[0065] As the manufacture approach of the water soluble dye of the betaine structure of having the above (1) or the structure expression of (2), the approach of specifically introducing betaine structure conventionally by the well-known approach, the approach indicated by 86th page - the 88th page of "completely revised version new and a guide to a surfactant" (work: Takehiko Fujimoto and Sanyo Chemical Industries, Ltd.) is mentioned to the water soluble dye expressed with the above-mentioned basic structure X.

[0066] Specifically, it is the intramolecular acidic group B about the above-mentioned 4th class ammonium structure as an inner salt machine nature machine. - In the case where carry out and a sulfonic group ( $-\text{SO}_3-$ ) is chosen, the approach explained below is used suitably.

[0067] First, to the water soluble dye of the above-mentioned basic structure X, tertiary amine (tertiary amine) structure is conventionally introduced by the well-known approach, and a heterocycle type water-soluble-dye amine as shown in a chain type water-soluble-dye amine as shown in the following structure expression (3), or a structure expression (4) is obtained. In addition, if water soluble dye includes amine structure from origin, it can be used as it is.

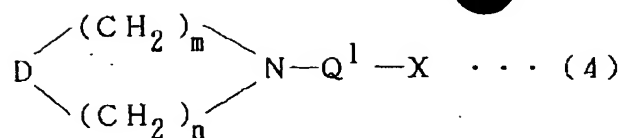
[0068]

[Formula 3]



[0069]

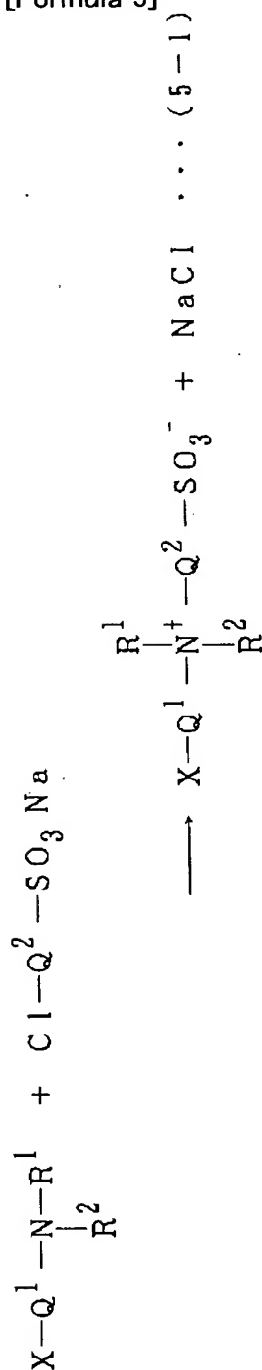
[Formula 4]



[0070] Next, the water-soluble-dye amine of one of the above and chloro alkyl sulfonic-acid sodium of carbon numbers 1-4, Or chloro alkyloxy sulfonic-acid sodium (any compound expresses with Cl-Q<sup>2</sup>-SO<sub>3</sub> Na) is added and mixed in a suitable solvent, if . while stirring at 60-80 degrees C for several hours — the following reaction formula (5-1) — a reaction is advanced, a sulfonic group is introduced into tertiary amine structure, and or (5-2) obtains the betaine structure.

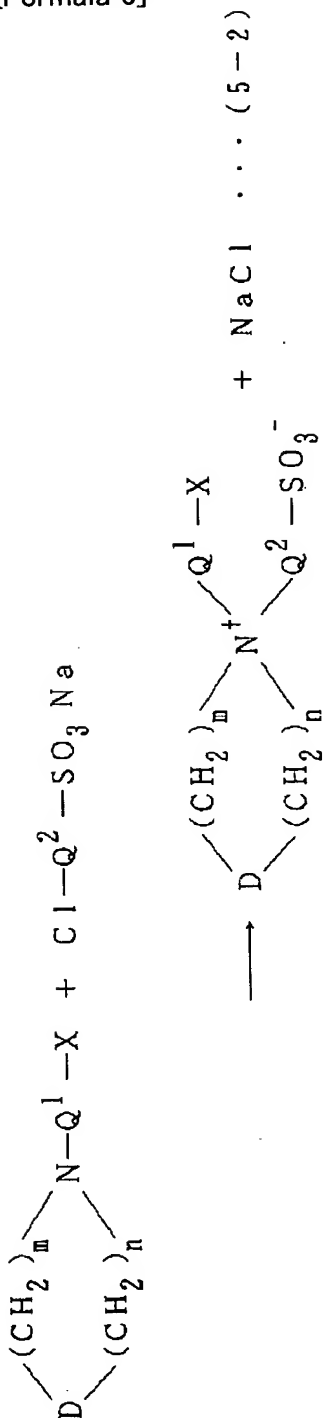
[0071]

[Formula 5]



[0072]

[Formula 6]



[0073] In addition, in the gestalt of this operation, it may express as "betaine-ization" introducing betaine structure to the water soluble dye expressed with the above-mentioned basic structure X. moreover, the water soluble dye into which betaine structure was introduced is expressed as a "betaine(name of water soluble dye)-ized derivative", or "a derivative (name of water soluble dye)" (for example, an "acid yellow 23 betaine-ized derivative" — or it is only expressed as "acid yellow 23 derivative").

[0074] Moreover, like the betaine structure where it is used by this invention, although the above-mentioned betaine which forms inner salt exists as one dipolar ion in a water solution, it may usually include in a betaine what is divided into a cation anion in a water solution. Since a cation will exist during the presentation of this ink and the fall of shelf life and generating of a Kogation will be invited

as a matter of fact like conventional ink when ink is prepared like the latter here using what is divided into a cation anion in a water solution, it is not desirable.

[0075] It will not be limited especially if the part which dissociates to ion in an aqueous solvent and serves as a cation (cation) as a cationic surface active agent contained in the color ink concerning this invention as an indispensable component is the matter in which surface activity is shown.

Therefore, each cationic surface active agent it is well-known that it can be used for the ink for ink jets is applicable to this invention.

[0076] Specifically, an amine salt, quaternary ammonium salt, sulfonium salt, phosphonium salt, carboxy betaine, aminocarboxylate, lecithin, SAPAMINA (Ciba-Geigy make), AKOBERUG (made in Arnold Hoffmann), etc. can be mentioned. Also in the above, an amine salt and quaternary ammonium salt are desirable, and the acetate (amine acetate) of amines, the acetate of the 4th class ammonium, or a chloride salt is more desirable especially.

[0077] As an example of the acetate of amines, the for example longest hydrophobic group is an alkyl group of carbon numbers 12-18 within the limits, and the acetate of the amines chosen from primary amine, secondary amine, tertiary amine, and the group that consists of those mixture etc. is mentioned preferably. As acetate of such amines, lauryl amine acetate etc. is mentioned, for example.

[0078] If the carbon number of the above-mentioned hydrophobic group becomes 11 or less, hydrophobicity will fall and it will be easy to become a hydrophilic property. On the other hand, if a carbon number becomes 19 or more, hydrophobicity will improve too much. That is, when the carbon number of the above-mentioned hydrophobic group separates from within the limits of 12-18, the balance of the hydrophilic group as a cationic surface active agent and a hydrophobic group collapses, and it is the good surface activity effectiveness.

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EXAMPLE

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[Example] Hereafter, although this invention is further explained to a detail based on an example and the example of a comparison, this invention is not limited to these. In addition, in the following explanation, the weight section is only written as the "section" and weight % is also only written as "%."

[0129] Moreover, the following approach estimated color bleeding, a Kogation, and shelf life.

[0130] [Color bleeding] It checked visually whether the blot between different colors at the time of forming an image in a PPC form etc. would occur using the color ink jet printer of a commercial thermal head method, and the boundary of each color would be indefinite. At this time, a blot etc. did not occur at all, but O, a blot, etc. generated the case where the boundary of each color was clear, and the case where the boundary of each color was indefinite was evaluated as x.

[0131] [Kogation] Like evaluation of color bleeding, using the color ink jet printer of a thermal jet method, it was filled up with each color ink to the amount of conventions of an ink cartridge, and the actuation which exhausts each color ink of all by image formation was repeated twice. It checked visually whether at this image formation time, the blur etc. would have occurred in the image. Then, the cartridge was decomposed and the heater part of a thermal head was checked visually.

[0132] At this time, the case where abnormalities, such as a blur, were checked during O and image formation in the case where an unusual condition is not seen at all almost similarly [ before abnormalities, such as a blur, are not checked during image formation and a heater part carries out image formation ], or a certain affix etc. was seen was evaluated as x.

[0133] [Shelf life] Like color bleeding and evaluation of a Kogation, using the color ink jet printer of a thermal jet method, it was filled up with each color ink to the amount of conventions of an ink cartridge, and was kept in the condition as it is for three months by ordinary temperature. Then, the same usual image formation as storage before was carried out using this ink cartridge. And it evaluated about the following three points.

[0134] 1. It is before and after storage of color ink, and the image formation actuation above-mentioned image formation actuation was compared. At this time, the regurgitation of a head to the color ink could not be carried out, but the case where it was not different from before \*\* and storage at all, and the case of good image formation where a blur is seen was completed in the image formed in the case where image formation cannot be carried out after [ although image formation was completed once, ] carrying out image formation to some extent, x and was evaluated as O.

[0135] 2. After ending the image formation actuation after heater storage of a thermal head, the cartridge was decomposed as well as evaluation of a Kogation, and the heater part of a thermal head was checked visually. Almost similarly [ before a heater part carries out image formation ] at this time, the case where O, a certain affix, etc. were seen in the case where an unusual condition is not seen was evaluated as x in any way.

[0136] 3. After ending the image formation actuation after condition storage of ink, the condition of color ink itself was checked visually. At this time, the case where O and a certain aggregate had generated the case where it is not different from before storage and neither coagulation nor precipitate has arisen was evaluated as x.

[0137] The shelf life of color ink was evaluated by synthesizing three above-mentioned evaluations. That is, the case where there was at least one x among the \*\* and above-mentioned three

evaluations of the case where there is one or \*\* among the O and above-mentioned three evaluations of the case where all three above-mentioned evaluations are O was evaluated as x.  
 [0138] [Example 1] In this example, the black ink of the presentation shown in Table 1 and cyanogen, a Magenta, and each color ink of yellow were prepared as an ink set concerning this invention, and image formation was performed using these ink set.

[0139] That is, while using the styrene-acrylic-acid copolymer as a dispersant and using the polyurethane emulsion for carbon black MA 7 (Mitsubishi Chemical make) as a binder as a black pigment, it blended so that it might become pure water (ion exchange water) and the content which shows these in Table 1, using 2-pyrrolidone, the diethylene-glycol monobutyl ether, trimethylol propane, and 2-propanol as other water-soluble organic solvents as a solvent, and the black ink (1) concerning this invention was prepared. pH of this black ink (1) is about 8, and showed alkalescence.

[0140] Next, it is if it will be in charge of preparation of the color ink of cyanogen first if preparation of color ink is explained, Using the direct blue 199 (DAIWA formation make) and the acid blue 9 (DAIWA formation make) as water soluble dye, betaine structure was conventionally introduced by the well-known approach (refer to the gestalt of said operation) to each [ these ] color, and the direct blue 199 betaine-ized derivative and acid blue 9 betaine-ized derivative as water soluble dye which has the betaine structure where it is used for this invention were obtained.

[0141] If similarly in charge of preparation of the color ink of a Magenta, using acid red 52 (DAIWA formation make) and the reactive red 180 (Clariant make) as water soluble dye, betaine structure was conventionally introduced by the well-known approach to each [ these ] color, and the acid red 52 betaine-ized derivative and reactive let 180 betaine-ized derivative as water soluble dye which has the betaine structure where it is used for this invention were obtained.

[0142] If similarly in charge of preparation of the color ink of yellow, using the acid yellow 23 (DAIWA formation make) as water soluble dye, betaine structure was conventionally introduced by the well-known approach, and the acid yellow 23 betaine-ized derivative as water soluble dye which has the betaine structure where it is used for this invention was obtained.

[0143] In addition to each above-mentioned betaine-ized derivative, using lauryl amine acetate as a cationic surface active agent, further, as a solvent, it blended with pure water (ion exchange water) so that it might become the content which shows these in Table 2, using 2-pyrrolidone, trimethylol propane and 1,5-pentanediol, or a diethylene glycol as other water-soluble organic solvents, and cyanogen, a Magenta, and each color ink (1) of yellow were prepared. pH of each [ these ] color ink (1) is about 5-6, and all showed the acescence.

[0144]

[Table 1]

		成 分 名	含有量 (重量%)
黒色顔料		カーボンブラックMA7	5
分散剤		スチレン-アクリル酸共重合体	1
結着剤		ポリウレタンエマルジョン	2
水性 溶媒	水溶性有機溶剤	2-ピロリドン	6
		ジエチレングリコールモノブチルエーテル	6
		トリメチロールプロパン	6
		2-プロパノール	2
	水	純 水	(残 量)
計		ブラックインク(1)	100

[0145]

[Table 2]

	シアンインク (1)		マゼンタインク (1)		イエローインク (1)	
	成分名	含有量 (重量%)	成分名	含有量 (重量%)	成分名	含有量 (重量%)
水溶性染料の ベタイン化 誘導体	ダイレクトブルー 199 誘導体	2	アシッドレッド 52 誘導体	0.5	アシッドイエロー 23 誘導体	2.5
	アシッドブルー-9 誘導体	1	リアクティブレッド 180 誘導体	2.5		
カチオン 界面活性剤	ラウリルアミン酢酸 塩	2	ラウリルアミン酢酸 塩	2	ラウリルアミン酢酸 塩	3
水性溶媒	トリメチロールプロ パン	6	トリメチロールプロ パン	6	トリメチロールプロ パン	7
	2-ピロリドン	6	2-ピロリドン	6	2-ピロリドン	4
	1,5-ペンタンジオ ール	7	1,5-ペンタンジオ ール	7	ジエチレングリコー ール	4
水	純水	(残 量)	純水	(残 量)	純水	(残 量)
計		100		100		100

[0146] In addition, in above-mentioned after-mentioned Table 2, 4, and 5, the betaine-ized derivative of water soluble dye is only written as "the derivative (name of water soluble dye)." Moreover, although there is no publication a "derivative" in the water soluble dye indicated to the after-mentioned Table 6 and 7, this shows that it is water soluble dye with the origin which does not introduce betaine structure, and differs from the above-mentioned betaine-ized derivative.

[0147] The ink cartridge of head one apparatus in the color ink jet printer of the thermal head method mentioned above was filled up with the above-mentioned black ink (1). Moreover, it was filled up with the above-mentioned cyanogen, a Magenta, and each color ink (1) of yellow until it became the amount of conventions at the ink cartridge of 3 color one apparatus and head one apparatus in the above-mentioned color ink jet printer.

[0148] As a recorded material, using the PPC form generally used, image formation was performed

using the above-mentioned ink cartridge until it consumed each above-mentioned color ink (1) completely. Furthermore, after that, it was filled up with each above-mentioned color ink (1) until it became the amount of conventions at the ink cartridge, and image formation was performed until it consumed each color ink (1) completely again.

[0149] Then, the image formed on the form was checked visually and it evaluated about color bleeding. Moreover, after image formation termination, the ink cartridge was decomposed, the heater part of an ink head was observed visually, and it evaluated about the Kogation. An evaluation result is shown in the after-mentioned table 8.

[0150] Furthermore, after keeping each above-mentioned color ink (1) for three months in the condition [ having filled up the ink cartridge ], image formation was performed like the above. The image with which it was formed [ with which were formed and it image-formation-operated ] after this storage was evaluated about shelf life by comparing storage before. An evaluation result is shown in the after-mentioned table 8.

[0151] [Example 2] In this example, the black ink of the presentation shown in Table 3 and cyanogen, a Magenta, and each color ink of yellow were prepared as an ink set concerning this invention, and image formation was performed using these ink set.

[0152] While using the polyurethane emulsion as a binder, using commercial self-distributed carbon black "KYABO jet" (a trade name, Cabot make) as a black pigment, it blended so that it might become pure water (ion exchange water) and the content which shows these in Table 3, using 2-pyrrolidone, the diethylene-glycol monobutyl ether, polyethyleneimine, and 2-propanol as other water-soluble organic solvents as a solvent, and the black ink (2) concerning this invention was prepared. pH of this black ink (2) is about 8, and showed alkalescence.

[0153] Next, if first in charge of preparation of the color ink of cyanogen when preparation of color ink was explained, using the acid blue 7 (DAIWA formation make) as water soluble dye, betaine structure was conventionally introduced by the well-known approach, and the acid blue 7 betaine-ized derivative as water soluble dye which has the betaine structure where it is used for this invention was obtained.

[0154] If similarly in charge of preparation of the color ink of a Magenta, using acid red 52 (DAIWA formation make) and the reactive red 58 (DAIWA formation make) as water soluble dye, betaine structure was conventionally introduced by the well-known approach to each [ these ] color, respectively, and the acid red 52 betaine-ized derivative and reactive let 58 betaine-ized derivative as water soluble dye which has the betaine structure where it is used for this invention were obtained.

[0155] If similarly in charge of preparation of the color ink of yellow, using the acid yellow 23 (DAIWA formation make) as water soluble dye, betaine structure was conventionally introduced by the well-known approach, and the acid yellow 23 betaine-ized derivative as water soluble dye which has the betaine structure where it is used for this invention was obtained.

[0156] In addition to each above-mentioned betaine-ized derivative, using lauryl amine acetate as a cationic surface active agent, further, as a solvent, it blended with pure water (ion exchange water) so that it might become the content which shows these in Table 4, using polyethyleneimine, 2-pyrrolidone and 1,5-pentanediol, or a diethylene glycol as other water-soluble organic solvents, and cyanogen, a Magenta, and each color ink (2) of yellow were prepared. pH of each [ these ] color ink (2) is about 5-6, and all showed the acescence.

[0157]

[Table 3]



		成 分 名	含有量 (重量%)
黒色顔料		キャボジェット	5
分散剤		—	—
結着剤		ポリウレタンエマルジョン	2
水性 溶 媒	水溶性有機溶剤	2-ピロリドン	6
		ジエチレングリコールモノブチルエーテル	6
		ポリエチレンイミン	6
		2-プロパノール	2
	水	純 水	(残 量)
計		ブラックインク (2)	100

[0158]

[Table 4]

	シアインク (2)		マゼンタインク (2)		イエローインク (2)	
	成分名	含有量 (重量%)	成分名	含有量 (重量%)	成分名	含有量 (重量%)
水溶性染料の ペタイン化 誘導体	アシッドブルー7 誘導体	3	アシッドレッド52 誘導体	0.5	アシッドイエロー 23誘導体	2.5
			リアクティブレッド 58誘導体	2.5		
カチオン 界面活性剤	ラウリルアミン酢酸 塩	2	ラウリルアミン酢酸 塩	2	ラウリルアミン酢酸 塩	3
水性 有機溶媒	ポリエチレンイミン	6	ポリエチレンイミン	6	ポリエチレンイミン	7
	2-ピロリドン	6	2-ピロリドン	6	2-ピロリドン	4
	1,5-ベンタンジオ ール	7	1,5-ベンタンジオ ール	7	ジエチレングリコー ル	4
水	純水	(残 量)	純水	(残 量)	純水	(残 量)
計		100		100		100

[0159] The ink cartridge in the color ink jet printer of the thermal head method mentioned above was filled up with the above-mentioned black ink (2) and the above-mentioned cyanogen, a Magenta, and each color ink (2) of yellow like the example 1. And the same image formation as an example 1 was performed, and it evaluated about color bleeding, a Kogation, and shelf life. An evaluation result is shown in the after-mentioned table 8.

[0160] [Example 1 of a comparison] Black ink (1) was prepared like said example 1 (refer to Table 1). Moreover, cyanogen, a Magenta, and each comparison color ink (1) of yellow were prepared like said example 1 except having used sodium lauryl sulfate as an anionic surface active agent, without using for the color ink concerning this invention the cationic surface active agent which is an indispensable component. pH of each [ these ] comparison color ink (1) is about 8-9, and all showed alkalescence. The content of each component in each comparison color ink (1) is shown in Table 5.

[0161]

[Table 5]

	比較シアインク (1)		比較マゼンタインク (1)		比較イエローインク (1)	
	成分名	含有量 (重量%)	成分名	含有量 (重量%)	成分名	含有量 (重量%)
水溶性染料の ベタイン化 誘導体	ダイレクトブルー 1199 誘導体	2	アシッドレッド52 誘導体	0.5	アシッドイエロー 23 誘導体	2.5
	アシッドブルー9 誘導体	1	リアクティブレッド 180 誘導体	2.5		
アニオン 界面活性剤	ラウリル硫酸ナトリ ウム	2	ラウリル硫酸ナトリ ウム	2	ラウリル硫酸ナトリ ウム	3
水性 有機溶剤	トリメチロールプロ パン	6	トリメチロールプロ パン	6	トリメチロールプロ パン	7
	2-ピロリドン	6	2-ピロリドン	6	2-ピロリドン	4
	1,5-ペンタンジォ ール	7	1,5-ペンタンジォ ール	7	ジエチレングリコー ール	4
水	純水	(残 量)	純水	(残 量)	純水	(残 量)
計		100		100		100

[0162] Using the above-mentioned black ink (1) and comparison color ink (1), image formation was performed like said example 1, and it evaluated about color bleeding, a Kogation, and shelf life. Moreover, an evaluation result is shown in the after-mentioned table 8.

[0163] [Example 2 of a comparison] Black ink (1) was prepared like said example 1 (refer to Table 1). Moreover, cyanogen, a Magenta, and each comparison color ink (2) of yellow were prepared like said example 1 except not using for the color ink concerning this invention the water soluble dye which has the betaine structure which is an indispensable component. pH of each [ these ] comparison color ink (2) is about 5-6, and all showed the acescence. The content of each component in each comparison color ink (2) is shown in Table 6. In addition, each water soluble dye shown in after-mentioned Table 6 and 7 is the same as each water soluble dye before introducing the betaine structure in said example 1 as it was mentioned above.

[0164]

[Table 6]

	比較シアインク (2)		比較マゼンタインク (2)		比較イエローインク (2)	
	成分名	含有量 (重量%)	成分名	含有量 (重量%)	成分名	含有量 (重量%)
水溶性染料	ダイレクトブルー 199	2	アシッドレッド52	0.5	アシッドイエロー 23	2.5
	アシッドブルー9	1	リアクティブレッド 180	2.5		
カチオン 界面活性剤	ラウリルアミン酢酸 塩	2	ラウリルアミン酢酸 塩	2	ラウリルアミン酢酸 塩	3
水性 溶媒	トリメチロールプロ パン	6	トリメチロールプロ パン	6	トリメチロールプロ パン	7
	2-ピロリドン	6	2-ピロリドン	6	2-ピロリドン	4
	1,5-ペンタンジォ ール	7	1,5-ペンタンジォ ール	7	ジエチレングリコー ル	4
水	純水	(残 量)	純水	(残 量)	純水	(残 量)
計		100		100		100

[0165] Using the above-mentioned black ink (1) and comparison color ink (2), image formation was performed like said example 1, and it evaluated about color bleeding, a Kogation, and shelf life. Moreover, an evaluation result is shown in the after-mentioned table 8.

[0166] [Example 3 of a comparison] Black ink (1) was prepared like said example 1 (refer to Table 1). Moreover, in order to draw a Kogation, in the color ink of this invention, cyanogen, a Magenta, and each comparison color ink (3) of yellow were prepared like said example 1 except having used the magnesium nitrate or calcium nitrate as polyvalent metallic salt (cation salt) which is the component which is not added. pH of each [ these ] comparison color ink (3) is about 6-7, and all showed the acescence. The content of each component in each comparison color ink (3) is shown in Table 7.

[0167]

[Table 7]

	比較シアインク (3)		比較マゼンタインク (3)		比較イエローインク (3)	
	成分名	含有量 (重量%)	成分名	含有量 (重量%)	成分名	含有量 (重量%)
水溶性染料	ダイレクトブルー 199	2	アシッドレッド52	0.5	アシッドイエロー 23	2.5
	アシッドブルー9	1	リアクティブレッド 180	2.5		
ノニオン 界面活性剤	アセチレングリコー ル	2	アセチレングリコー ル	2	アセチレングリコー ル	3
多価金属塩	硝酸マグネシウム	3	硝酸マグネシウム	3	硝酸カルシウム	5
水性溶媒	トリメチロールプロ パン	6	トリメチロールプロ パン	6	トリメチロールプロ パン	7
	2-ピロリドン	6	2-ピロリドン	6	2-ピロリドン	4
	1,5-ベンタンジオ ール	7	1,5-ベンタンジオ ール	7	ジエチレングリコー ル	4
水	純水	(残 量)	純水	(残 量)	純水	(残 量)
計		100		100		100

[0168] Using the above-mentioned black ink (1) and comparison color ink (3), image formation was performed like said example 1, and it evaluated about color bleeding, a Kogation, and shelf life. Moreover, an evaluation result is shown in the following table 8.

[0169]

[Table 8]

		実施例 1	実施例 2	比較例 1	比較例 2	比較例 3
ブラック インク	種類	(1)	(2)	(1)	(1)	(1)
	pH	8	8	8	8	8
カラー インク	種類	(1)	(2)	比較(1)	比較(2)	比較(3)
	pH	5~6	5~6	8~9	5~6	6~7
	水溶性染料 のベタイン 化の有無	あ り	あ り	あ り	な し	な し
	界面活性剤	カチオン	カチオン	アニオン	カチオン	ノニオン
	多価金属塩	な し	な し	な し	な し	あ り
カラーブリード		○	○	×	○	○
コゲーション		○	○	○	×	×
保管 後	1. 動作	○	○	○	×	△
	2. ヒータ	○	○	○	×	×
	3. インク	○	○	○	×	○
保存性		○	○	○	×	×

[0170] It was possible to have attained prevention of color bleeding, prevention of a Kogation, and all the improvement in shelf life in the case where the ink set for ink jets concerning this invention is used so that clearly from the result of Table 8 (example 1-2). However, if betaine structure was not introduced into water soluble dye, shelf life falls upwards and generating of a Kogation was not able to be prevented, either (example 2-3 of a comparison). When the cation salt was used especially, shelf life got worse very much (example 2 of a comparison).

[0171] On the other hand, when introducing betaine structure into water soluble dye, prevention of a Kogation and improvement in shelf life could fully be attained, but (an example 1-2, example 1 of a comparison) if a cationic surface active agent was not used, generating of color bleeding could not be prevented but image quality deteriorated sharply (example 1 of a comparison).

[0172] Thus, in the ink for ink jets concerning this invention, since it has come to contain the water soluble dye which has betaine structure, and a cationic surface active agent in an aqueous solvent, it can consider as the outstanding ink which can attain prevention of color bleeding, prevention of a Kogation, and all the improvement in shelf life.

[Translation done.]

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